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14. ABSTRACT The most significant accomplishments were determining the conditions for preparing microcellular structural foams from high-temperature polymers of interest to the US Air Force. The primary system was rodlike polybenzobisthiazole blended with poly(etherketoneketone) with 5% rod content. This gave microcellular foams with densities about 0.92 g/cc, and a yield strength about 9.4 ksi. A modified foaming technique gave foams with high porosity, a density of 0.65 g/cc, and pore sizes from 10 to 40 μm. Also, some sulfonated poly(p-phenylenebenzobismidazole)/poly(2-vinylpyidine) molecular composites gave foams of uniform microstructures and a cell size less than 10 μm, but with some brittleness. Molecular composites based on polysulfone (PSF) and polybenzimidazole (PBI) were also successfully prepared. PSF and PBI are immiscible, but introduction of functional groups into the PSF or PBI resulted in miscible polymer blends. Very homogeneous microcellular foams were obtained from them, and their thermal behavior and mechanical properties were encouraging.

15. SUBJECT TERMS

High-temperature polymers, foams, mechanical properties, scanning electron microscopy

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Technical Final Report

STRUCTURAL FOAMS OF IMPROVED STRENGTH AND THERMAL STABILITY FROM RANDOM-COIL AND RIGID-ROD POLYMERS

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I. ABSTRACT

The main goal of this project was the preparation, characterization, and evaluation of polymer-based foams of sufficient toughness and high-temperature stability to be useful as structural materials in Air Force applications. A variety of thermoplastic polymers have been evaluated with regard to the extent to which they can be formed into monolithic foams, and methods have been developed for toughening these foams. The primary mechanism for improving toughness and other mechanical properties is inclusion of rigid-rod polymers as dispersed phases. Both thermoplastics and thermoplastic blends have been processed into the desired foams through extensions of the methods developed by Dr. Seng C. Tan and co-workers at Wright Materials Research Company (WMR), who were subcontractors in the project. Their foaming techniques are particularly interesting in that they can provide anisotropic alignment of the rigid-rod chains along the struts or walls making up the foam. Such alignment can produce large increases in mechanical properties, particularly toughness, as has been demonstrated in the case of graphitized carbon foams. In the present application, judicious choices of high-temperature thermoplastic polymers as the matrix materials have resulted in substantial improvements over materials now in use in aircraft, particularly with regard to thermal properties. Incorporation of the oriented rigid-rod polymers into the most promising of these thermoplastics has resulted in even greater increases in mechanical and thermal properties. The properties of primary interest for optimization are of a mechanical nature, and for the anticipated structural applications include modulus, ultimate strength, maximum compressibility, impact resistance, and toughness. The microstructural details of the foams have been monitored via standard microscopic techniques, and this has provided guidance for tailoring the conditions for the best foam processing.

II. BACKGROUND INFORMATION

II.1 General

Current military aircraft use large amounts of sandwich materials because of their superior relative stiffness, relative strength, and bending stiffness as compared to their solid counterparts. Most of the commercially available polymeric sandwich cores have temperature capabilities of up to only 350 °F, however. These structural foams are currently processed from polymers such as polymethacrylic imide and polyvinyl urea-amides. In these examples, there are several processing difficulties. For example, polymethacrylic imide foams (such as Rohacell) are manufactured by the hot foaming of methacrylic acid-methacrylonitrile monomers. Several steps are involved in this process and the blowing agent used is carbon monoxide, which is toxic. Some rigid foams also give off hazardous gases during the post-processing steps. For instance, "polyvinyl" foams give out HCl gas during machining stages.

Rigid-rods such as the 2-sulfo-PBIs have superior strength and modulus. When they are blended with thermoplastic resins they can significantly improve the T_g (glass transition temperature) and mechanical properties of the host matrix. In the past, molecular dispersion of the rigid-rod polymer in the molecular composite could be expected only for solutions below a rather low critical concentration C_{cr} (3-4 vol %); otherwise, there is extensive segregation of the rigid-rod polymers. Recent advances in this technology area by researchers at Wright Laboratory[1,2], however, permit incorporating up to 10% of the rigid-rod polymers without the phase separation problem, and without loss of the glass transition.

Specifically, in this research project rigid-rod benzobisazole polymers functionalized with pendant sulfonic acid groups were incorporated into thermally stable thermoplastic host matrices, in the production of light-weight structural polymer foams with superior mechanical and thermal properties.

II.2 Conventional Structural Foams

Many kinds of core materials and forms are available today for sandwich constructions in the aircraft and aerospace industry[3]. These include: wood, polystyrene foams, polyurethane foams, poly(vinyl chloride) (PVC) foams, poly(methacrylimide) (PMI) foams, polyimide foams, and honeycomb cores. Among these core materials, PVC foams, PMI foams, and aramid paper and aluminum honeycombs are most commonly used in this industry.

PVC foams are based on the same chemical family as that in the familiar garbage bags, plastic pipe, and plastic films in common use, but are produced using a quite different process. Divinycell, Klegecell, Termanto are representatives of this class of foams. Poly(methacrylimide) foams such as Rohacell are manufactured by hot foaming of methacrylic acid-methacrylonitrile copolymer sheets. During foaming this copolymer is converted to polymethacrylimide, as shown in Figure 1. Rohacell is recognized as a good performance structural foam, but only for applications up to 350 °F. In fact, the mechanical properties of all these polymeric rigid foams degrade significantly at elevated temperatures. As examples, the compressive strengths of Rohacell and Divinycell foams decrease to one-third of their original compressive strength at 350 °F, as shown in Figure 2 (where pcf refers to pounds per cubic foot). Long-term applications at this temperature are therefore not recommended.

Figure 3 presents comparisons among commercially available sandwich core materials for aircraft applications, with regard to the dependences of their compression strength on densities. The results reveal that Nomex aramid paper honeycombs are

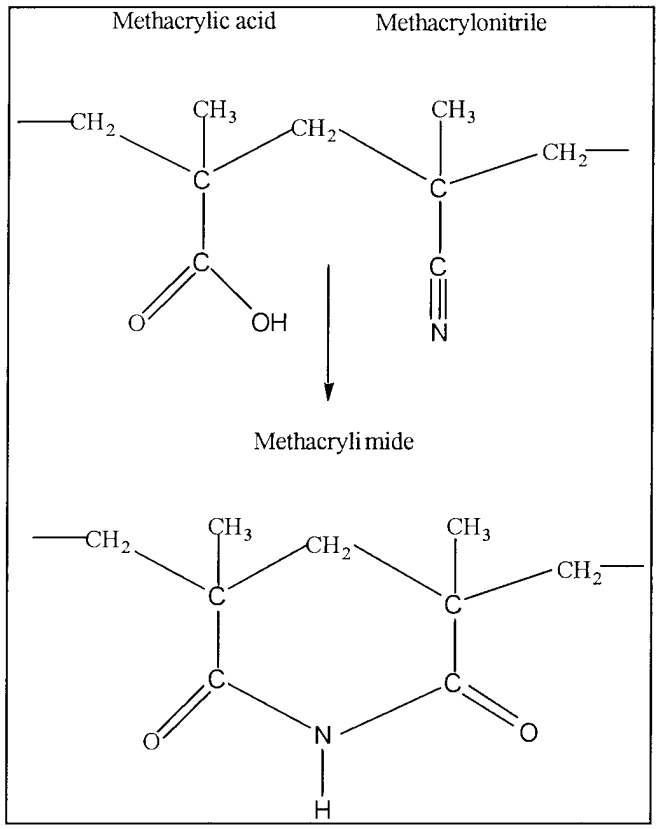


Figure 1. Formation of poly(methacrylimide) (PMI).

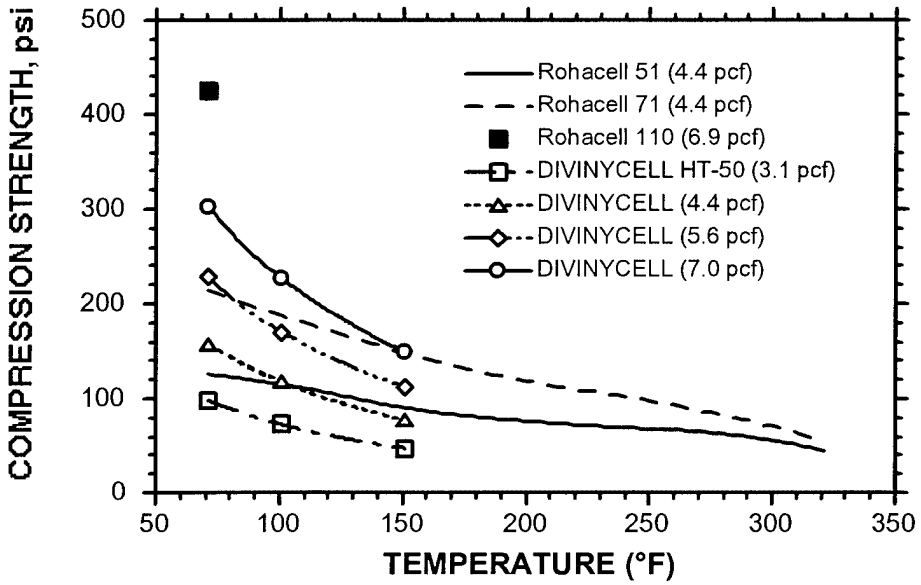


Figure 2. Compression strength as a function of temperature for some polymeric foams.

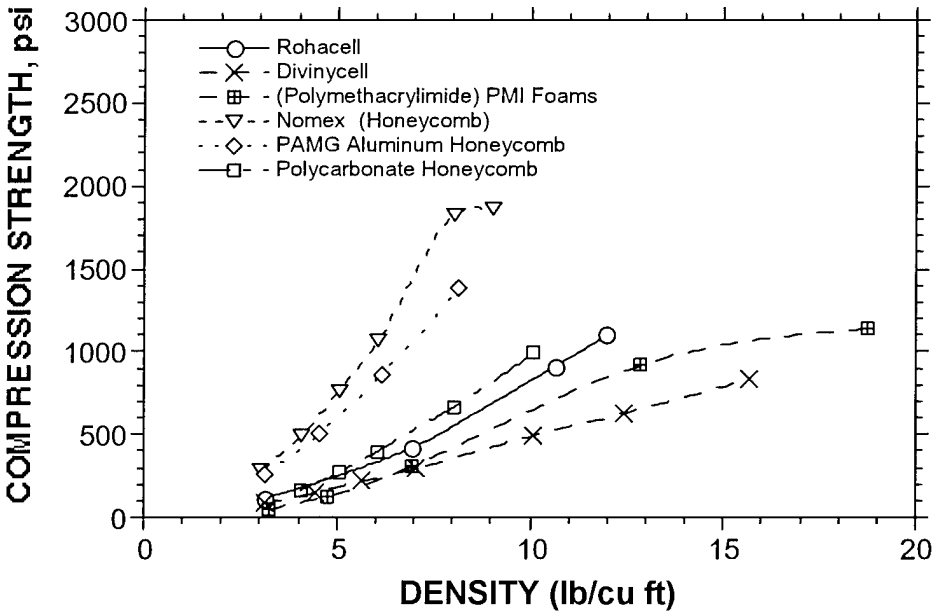


Figure 3. Compression strength as a function of density for some polymeric foams.

among the few that have acceptable ratios of extensional strength to weight. The drawbacks of these various honeycomb cores are their: (1) pronounced weakness in shear (a very important property in most applications of core materials), (2) moisture retention due to their open-cell constructions, and (3) high prices that limit their wide-spread utilization.

II.3 Microcellular Foaming Techniques

Foams from amorphous, glassy polymers such as polystyrene have been manufactured for decades. Most commercial polymer foams, however, are processed using a chemical blowing agent (CBA) which is decomposed during processing, or through the use of blowing gases such as the chlorofluorocarbons. The use of CBA's results in foams where the cell sizes are of the order of millimeters. The mechanical properties of these foams are usually much weaker (orders of magnitude) than those of the solid (unfoamed) polymers. To overcome the deficiencies of the conventional ("macrocellular") foams, Colton and Suh[4,5] proposed a processing approach for the preparation of "microcellular" foams. Such foams are defined as those having cell size the order of 10 μm and cell density in the range 10^9-10^{13} cells/cc. Such a process was, indeed, developed by Kumar and Suh[6]. Most of work until now has been restricted to amorphous polymer systems, though recently, the concept has been extended to semicrystalline polymers such as poly(ethylene terephthalate).

In recent years, this foaming principle was applied by engineers of the Wright Materials Research Co.[7-11] in the processing of foams from mesophase pitch, a carbon fiber precursor. They have overcome the poor solubility of the gas in this liquid crystalline pitch and successfully processed microcellular graphitic foams. In this process the pitch was melted in a pressure vessel by raising the temperature to ca. 300 °C. The experiments were carried out under a steady stream of nitrogen gas, and efforts were made to ensure uniform heating of the pitch disk. The disk was then saturated with a gas at high pressure. In the present case, the saturating gas was nitrogen and the pressure was applied for only a short period of time. The pressure and temperature were then dropped suddenly to obtain the desired foaming. The pitch foam was then oxygen stabilized, carbonized and graphitized. The cell sizes are of the order 50-100 μm and the struts are around 7-10 μm (similar to those of carbon fibers). Polarized light microscopy showed that there was alignment of the graphitic plane along the struts. This anisotropy gave rise to greatly improved mechanical properties.

II.4 Random-Coil Matrix Polymers

Thus, this project seeked to address the described problems, by developing foams with good thermal stability and having well controlled density (and hence pore microstructure and mechanical properties). This was done by foaming high-temperature, high-performance thermoplastics via the described new, proprietary foaming technique developed by the collaborators in this project. A number of classes of important high-termperature polymers for this project are readily accessible in that they are commercially available and are relatively inexpensive[12,13]. Examples are the polysulfones (Amoco Udel), and polyethersulfones (Amoco Radel). The typical properties of these thermoplastics include toughness at high temperatures, hydrolytic stability, and good chemical resistance. As a result, typical applications include lighting fixtures, electrical/electronic, medical devices, chemical process equipment, automotive, and food service uses. In fact, open-cell polysulfone membranes, with cell sizes on the order of 10 μm are already fabricated for general filtration uses. Thus, these candidates seem eminently suitable for forming stable foamed structures.

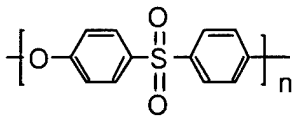
II.5 Rigid-Rod Reinforcing Polymers

Particular attention was also paid to several high-temperature polymers of special interest to the AFOSR, such as polybenzobisoxazoles (PBO)[14-20], polybenzobisthiazoles (PBZT)[19-22], and sulfonated poly(p-phenylenebenzobismidazole)(SPBI) to make them more tractable and bondable to various matrix materials[23-32]. These materials act as both filler and as an intimatedly bonded composite phase to increase the toughness and the thermal resistance of a thermoplastic phase. Having them aligned along the foam struts should be particularly effective with regard to improving mechanical properties. This work was carried out in collaboration with Dr. F. E. Arnold of the Polymer Branch at the Wright Patterson Air Force Base.

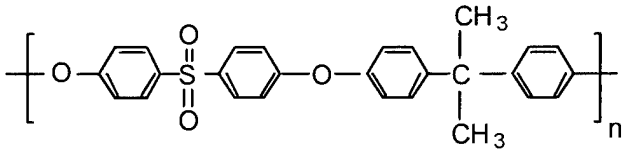
The structures of some of the polymers mentioned are shown on the following page.

Thermoplastic Matrix Phases

Polyethersulfone
PES
Radel ®

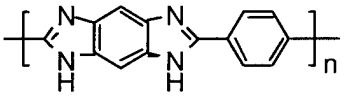


Bisphenol A polysulfone
Udel ®

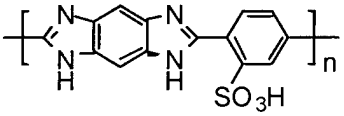


Rigid Rod Polymers

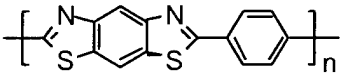
Polybenzimidazole
PBI



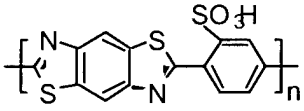
Sulfopolybenzimidazole
2-Sulfo-PBI



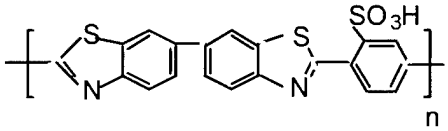
Polybenzobisthiazole
PBT



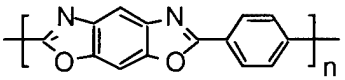
Sulfopolybenzobisthiazole
SPBT



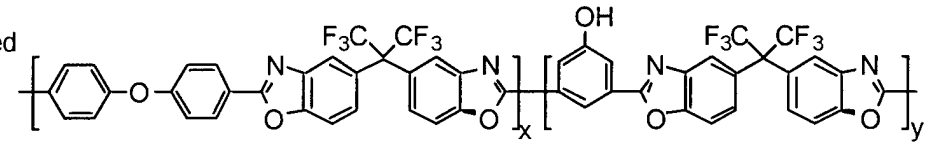
Sulfobiphenylpolybenzobisthiazole
SBPPBT



Polybenzobisoxazole
PBO



Hydroxy functionalized copolymer of polybenzoxazole
HPBO



III. Preparation of Molecular Composites and Foams

The main purposes of this research was to develop more environmentally friendly foam processing techniques, to enhance the temperature and mechanical properties of the structural foams, and to maintain low observability characteristics for military applications including supersonic fighters and spacecraft. This was accomplished by means of a microcellular foaming technique for rigid-rod molecular composites, using a single-step operation. The technique did not use or release any hazardous chemicals/gases. More specifically, it employed innocuous gases such as nitrogen, with the foaming occuring through the establishment of simple thermodynamic instabilities in the system, as described below. Mechanical properties of the foams were enhanced through incorporation of rigid-rod polymers such as functionalized polybenzobisazoles, which have superior strength and modulus. Blending them into a host thermoplastic resin will significantly increase its T_g and mechanical properties. Structural foams made by such high performance polymer systems would have many applications in Air Force weapon systems.

As already mentioned, conventional foaming techniques for polymers use chemical blowing agents that result in bubbles with diameters the order of millimeters. This is a great disadvantage, since it is known that the mechanical properties of structural foams are inversely proportional to the bubble size. That was the primary reason for proposing a foaming technique for preparing microcellular foams, including those having rigid-rod polymers in composite materials. In some cases, the rigid rods are dispersed almost to the molecular level, resulting in the descriptor "molecular composites". Such foamed rigid-rod molecular composites should have superior thermal and mechanical properties, making them high-performance materials. These microcellular foams would be new lightweight materials possessing many potential applications in the military.

Technically this was a challenging project. First, the blend of rigid-rod and thermoplastic random-coil matrix tends to give rise to phase separation problems. Second, rigid-rod polymers do not have an accessible T_g. The first problem has been solved recently by researchers at Wright Laboratory[1] using the approach of rigid-rod benzobisazole polymers functionalized with pendant sulfonic acid groups. These sulfo-pendant rigid-rods can form ionic associations with polar thermoplastic matrix polymers that have basic functionalities. The repulsion between ionically charged rigid-rods can prevent aggregation of the rods that normally lead to phase separation in the matrix. This approach provides a mechanism by which phase separation during the processing of the

molecular composite can be prevented above the C_{cr} (critical concentration, 3-4 vol %). The second problem can be alleviated by blending rigid-rods with thermoplastic matrices which do have accessible glass transitions. Wright Laboratory's research results[1] showed that up to 10 wt % of rigid-rod polymer could be incorporated in a thermoplastic polymer without loss of a glass transition. The T_g of a commercially available poly(4-vinylpyridine) was increased from 153 to 210 °C (37 % improvement) by the addition of only 10% of poly(p-phenylenebenzobisimidazole) with a sulfonic acid pendant ("2-sulfo-PBI"). The storage modulus was also increased considerably as a result of this rigid-rod incorporation.

III.1 Molecular Composites

The polybenzobisthiazole (PBZT) and 2-sulfo-PBI rigid-rod polymer are ideal candidates for forming molecular composites for this research and can be obtained at relatively high molecular weights[1]. (They typically have an intrinsic viscosity between 4.0 and 7.0 dl/g in methanesulfonic acid at 30 °C). Another advantage of the SPBI is the fact that it can be solubilized as its triethylammonium salt in alcohol. A good candidate for the host matrix phase was commercially available thermoplastic poly(etherketoneketone) or polyethersulfone, for which T_g is about 156°C or 220 - 260°C, respectively. The chemistry of this class of molecular composite is illustrated in Figure 4. If the same improvement in T_g were obtained for this 2-sulfo-PBI/polyethersulfone molecular composite as was the case for 2-sulfo-PBI/poly(4-vinylpyridine), then one should expect a T_g in the range 300 - 360 °C.

The polybenzobisthiazole (PBZT) and poly(p-phenylenebenzobisimidazole) with a sulfonic acid pendant (SPBI) were synthesized and provided by Dr. F. E. Arnold of the Wright Laboratory. The PBZT and SPBI were blended with a number of matrices, including poly(etherketoneketone) (PEKK), to form rigid-rod molecular composites.

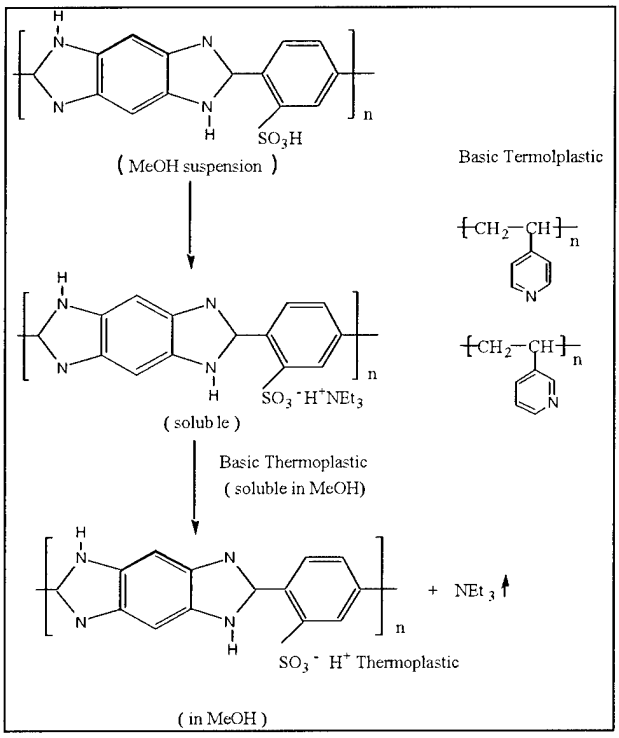


Figure. 4. Rigid-rod thermoplastic molecular composite formation via ionic interchange.

The starting materials for the blending of PBZT/PEKK molecular composites include:

- Poly (*p*-phenylene-benzobisthiazole) (PBZT), processed from PBT dope containing 82.85% P_2O_5, Intrinsic Viscosity (IV) = 21.4 and 14.0 dl/g
- Polyetherketone-ketone (PEKK), linear PEKK >99%, Density (D) = 1.0g/cc.
- Methanesulfonic acid (CH_3SO_3H), 99%, D = 1.481g/cc.
- Ammonium hydroxide (NH_4OH), 28.0~30.0%, D = 0.90g/cc.

For the preparation of PBZT/PEKK molecular composites, these raw polymeric materials were put in a vacuum oven to dry at 120°C before use. The experimental setup is illustrated in Figure 5. It basically included a mechanical stirrer with controller, oil bath and hot plate. Blending procedures are shown in Figure 6. Both the PBZT and PEKK were dissolved in methane sulfonic acid. After precipitation in distilled water they

became fibrous materials. They were then neutralized in ammonium hydroxide and vacuum dried.

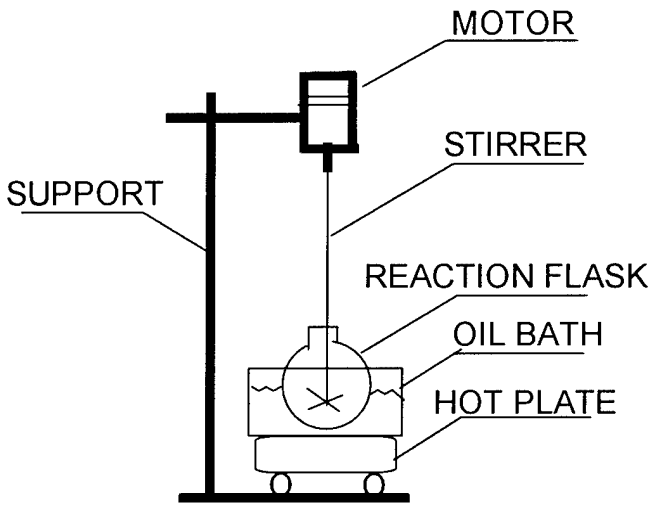


Figure 5. The equipment setup for the preparation of molecular composites.

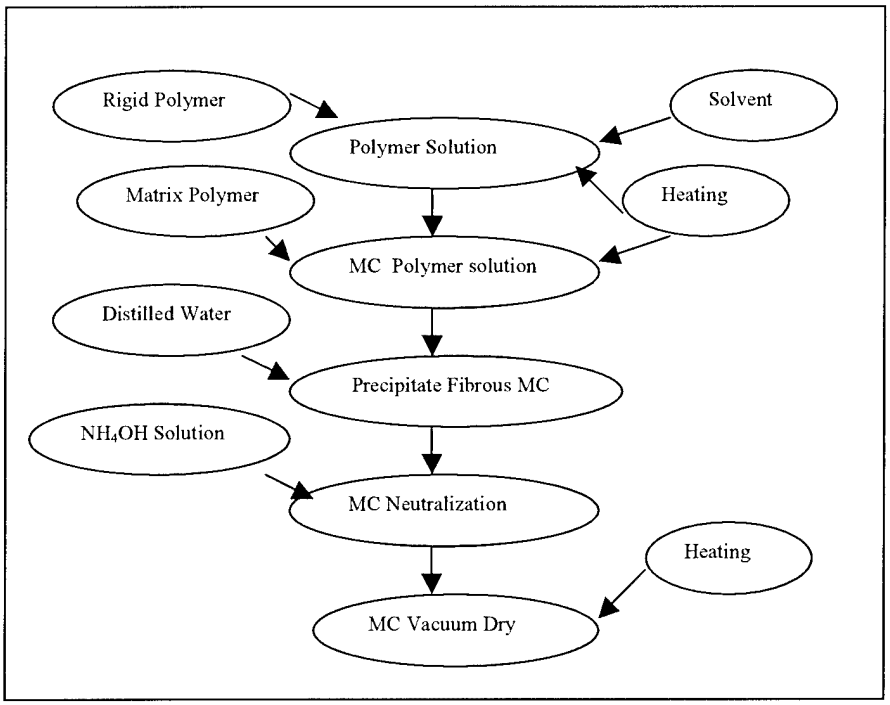


Figure 6. Preparation procedure for the PBZT/PEKK molecular composites.

The color of the PBZT/PEKK molecular composites became darker when the percentage of the PBZT was increased, as shown in Figure 7. The molecular composites with 10/90, 30/70, and 50/50 percent PBZT/PEKK were blended during the first two years of this project whereas 5/95 percentage of MC was blended during the third year. A PBZT/PEKK molecular composite with lower percent PBZT was yellow, as shown in Figure 8.

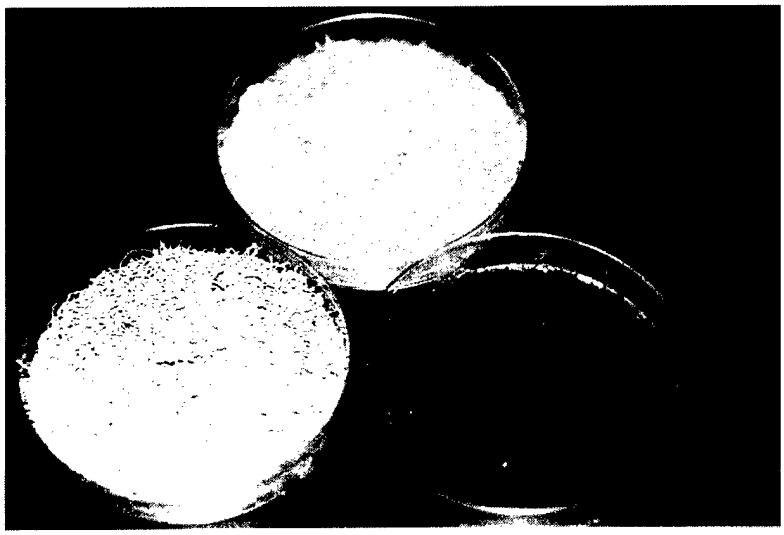


Figure 7. Molecular composites with various percentages of PBZT: top (10/90), bottom left (30/70) and bottom right (50/50).

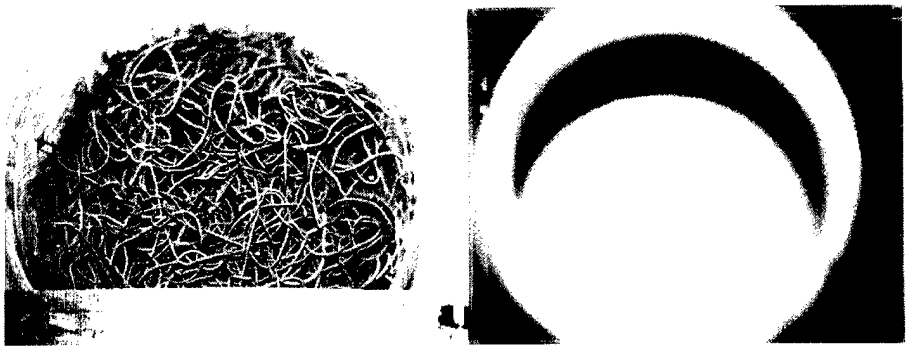


Figure 8. Molecular composites with 5/95 % PBZT/PEKK.

III.2 Microcellular Foams from Molecular Composites

The rigid-rod molecular composites, PBZT/PEKK and sulfonated poly(p-phenylenebenzobismidazole)(SPBI)/poly(2-vinylpyidine)(P2VP), were ground into fine powders and compression molded into disks. The thicknesses of the samples were varied by using different amounts of the polymers.

The compression-molded samples were then foamed in a pressure vessel, using the patented foaming process developed by WMR. A schematic diagram is shown in Figure 9.

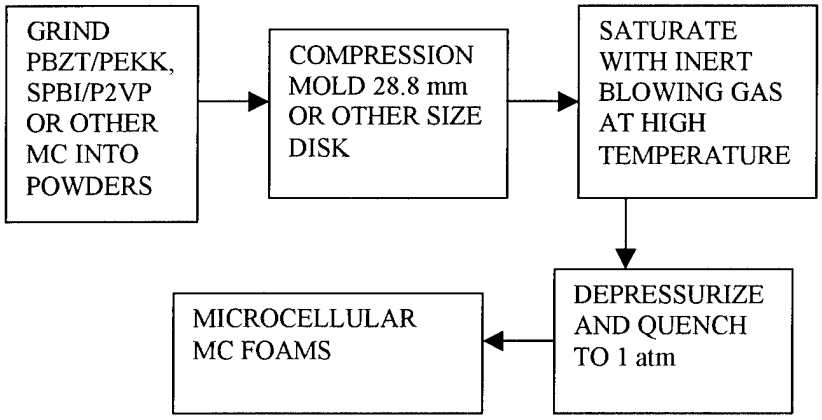


Figure 9. Schematic of WMR's proprietary foaming process.

During the course of this research, we found that PBZT/PEKK molecular composites with 10 to 50% PBZT were very rigid and very difficult to foam. Therefore, we also blended a PBZT/PEKK molecular composite with 5% of PBZT. Unfortunately, even 5% of PBZT resulted in rigidity. Experimental observations indicated that this class of molecular composites softened very little at elevated temperatures.

Dr. Arnold synthesized the SPBI/P2VP molecular composites. Two batches were prepared, one containing 5% and another containing 10% of SPBI rigid rods. The first could not be foamed or consolidated after many trials. We then tried to process it using a compression molding technique, which also failed to give consolidation. Dr. Arnold looked into this problem and found that the material was contaminated during the synthesis.

Thin films cast from a solution of this molecular composite were successfully foamed at UC. The scanning electron microscopy (SEM) results showed that their microstructures were very uniform and the cell size was less than 10 μm. The relative density and cell size were tailored by varying the foaming conditions. After precipitation, the molecular composite can no longer be dissolved in solvents. WMR did foam the 10/90 SPBI/P2VP molecular composite using the proprietary foaming technique. The material did foam but it was quite brittle, as least considerably more brittle than the PBZT/PEKK molecular composite.

IV. PROPERTIES OF MOLECULAR COMPOSITES AND FOAMS

Experimental results described in this report include TGA, and DSC analyses of the polymers and molecular composites, photographs, SEM analyses, and compression stress-strain relationships of the foams from these materials.

IV.1 Analyses of Materials and Foams

The constituents of the molecular composites had the following properties:

PEKK

- Melting point: 310 – 350 °C
- T_g: 156 °C
- % Volatiles: 0.7 wt%
- Solubility in water: insoluble
- Coefficient of thermal expansion: 77 μm/m°C
- Decomposition temperature: 400 °C
- Thermal conductivity (60 - 213°C): 0.25 W/mK

Poly(2-vinylpyridine) (P2VP)

- T_g: 107 °C
- Softening point: 200 °C

PBZT Rigid-rod, no T_g

TGA analysis of the PEKK polymer, Figure 10, indicated that this material decomposed at about 525°C. TGA analyses of PBZT/PEKK with 10/90, 30/70, and 50/50 ratios revealed that they had a little decrease in weight between 330 and 380 °C but were not decomposed up to the testing temperature of 600 °C; see Figures 11 – 13. DSC analyses of the PEKK polymer showed that its T_g was about 156 °C (Figure 14). DSC results on the10/90 PBZT/PEKK molecular composite indicated that its T_g was about 230°C. Therefore, the addition of rigid rods in a molecular composite did increase the T_g of its matrix material. DSC analysis of P2VP indicated that its T_g was about 107 °C (Figure 16). The addition of 10% SPBI into the SPBI/P2VP molecular composite increased its T_g only marginally. TGA of this rod/coil composite indicated, after 2-4 wt%

loss due to absorbed moisture (RT-200°C), that there was no thermal degradation until around 330°C in helium and 320°C in air.

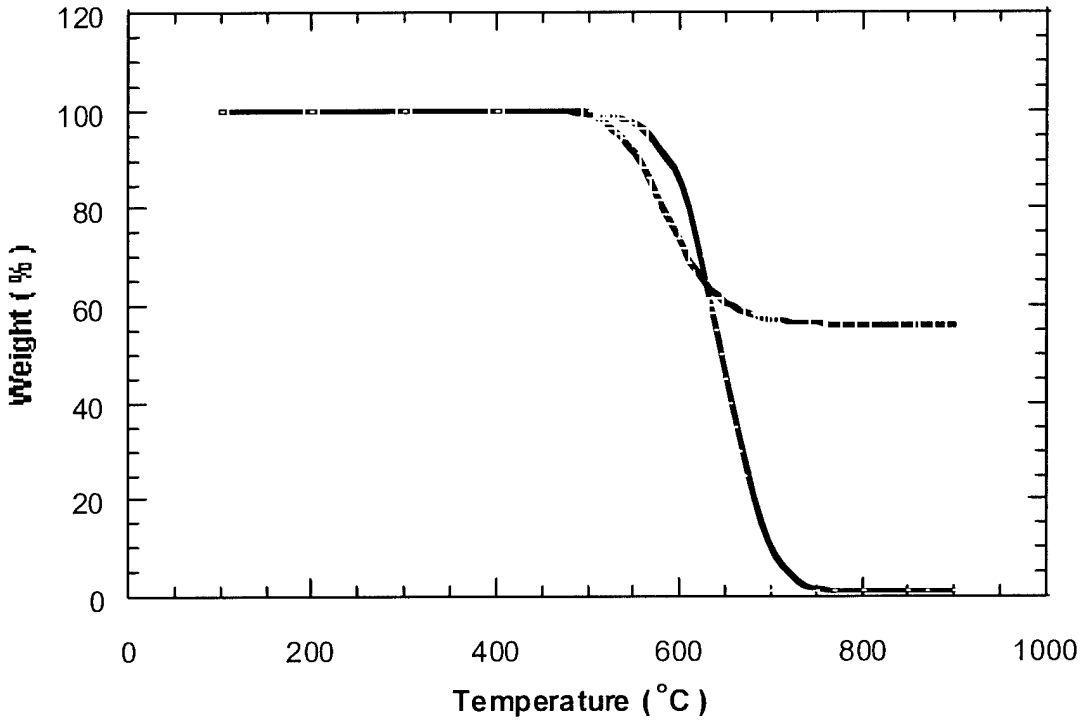


Figure 10. TGA analysis of the PEKK polymer.

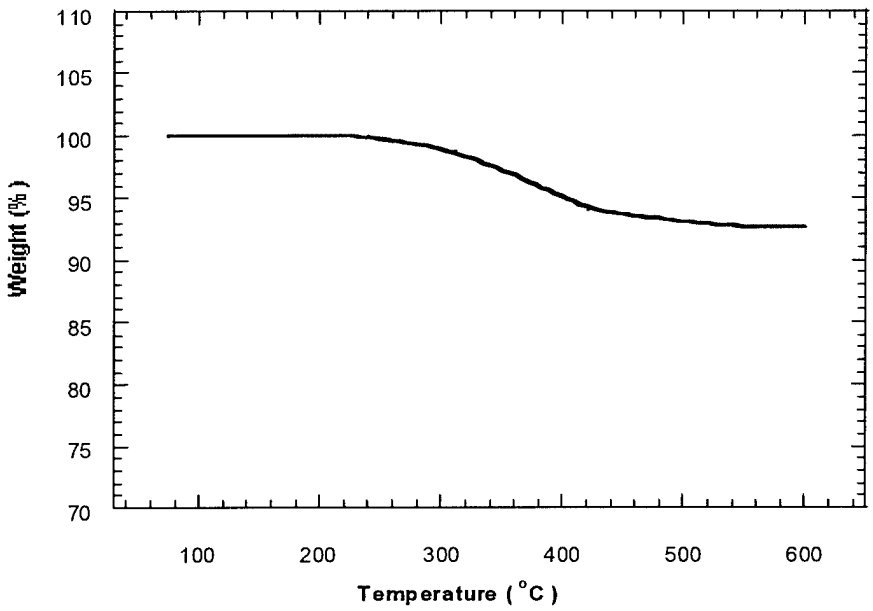


Figure 11. TGA analysis of 10/90 the PBZT/PEKK molecular composite.

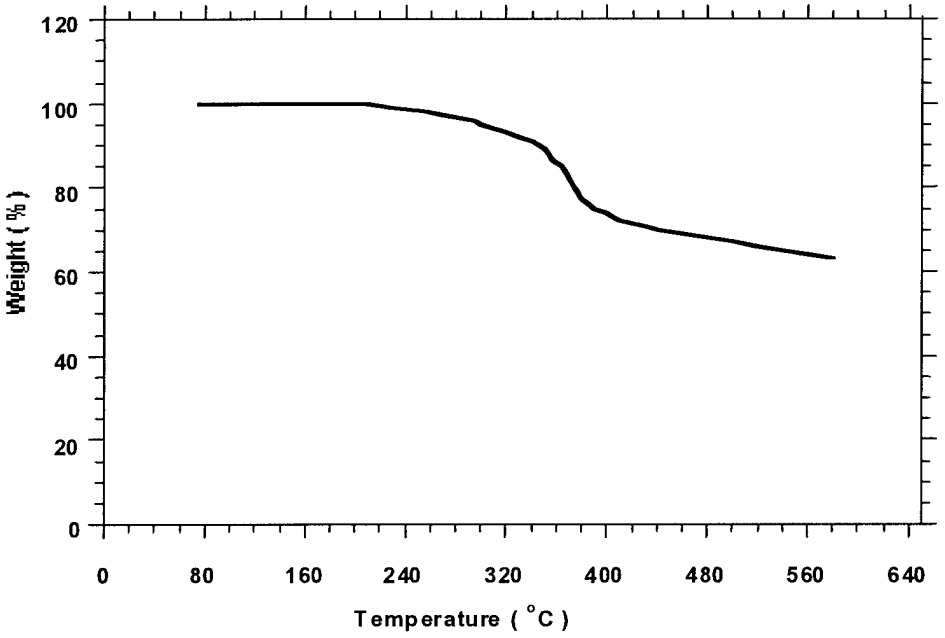


Figure 12. TGA analysis of 30/70 the PBZT/PEKK molecular composite.

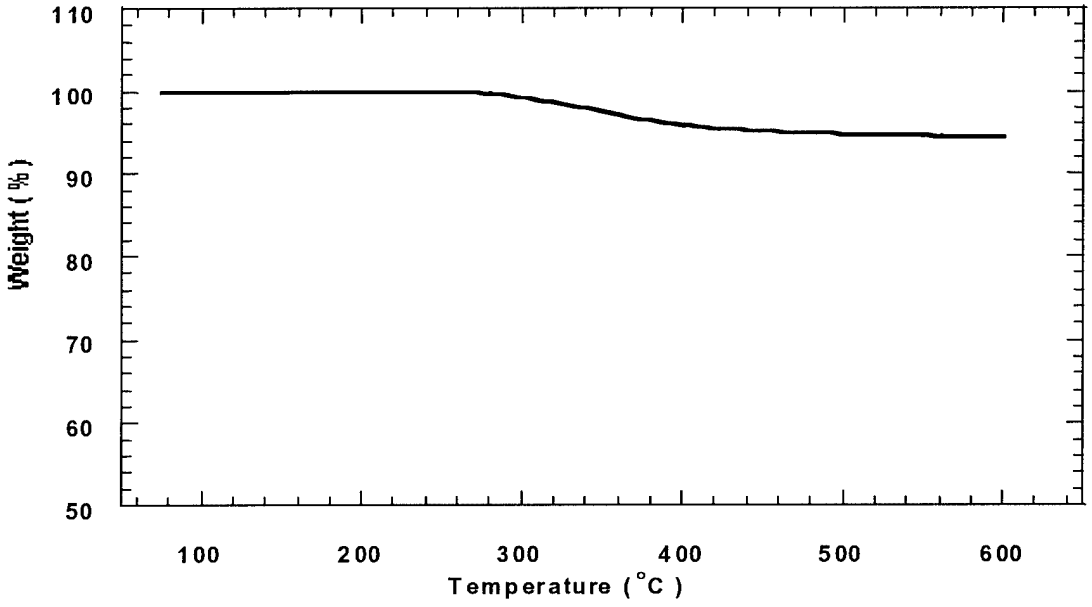


Figure 13. TGA analysis of 50/50 the PBZT/PEKK molecular composite.

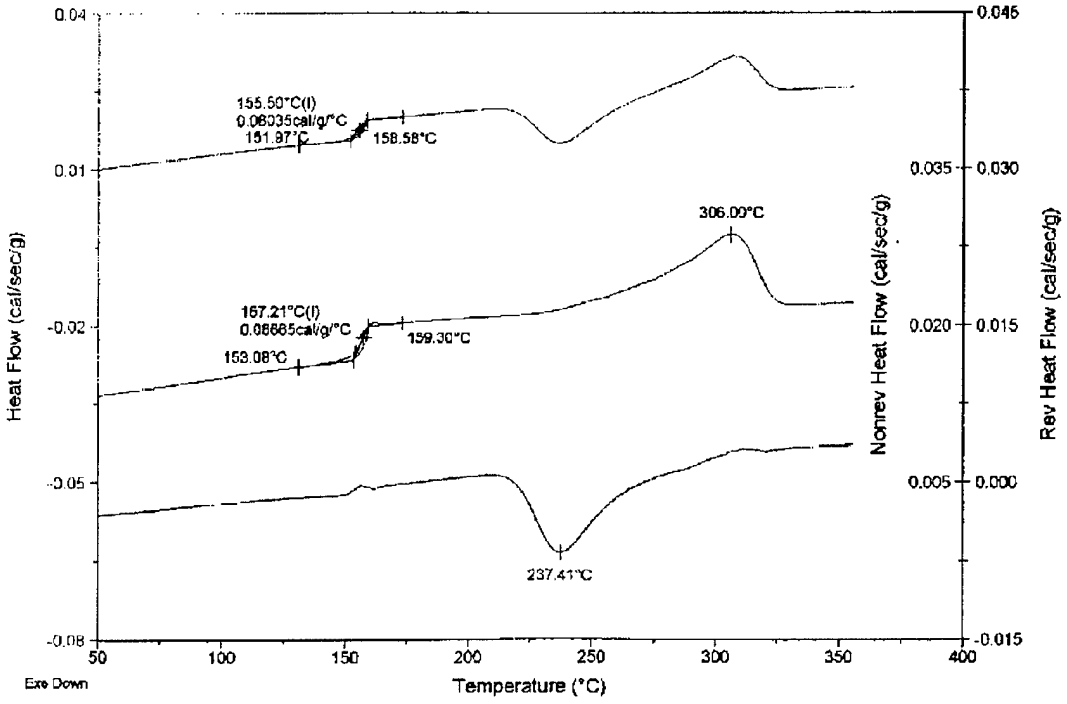


Figure 14. DSC analysis of the PEKK polymer.

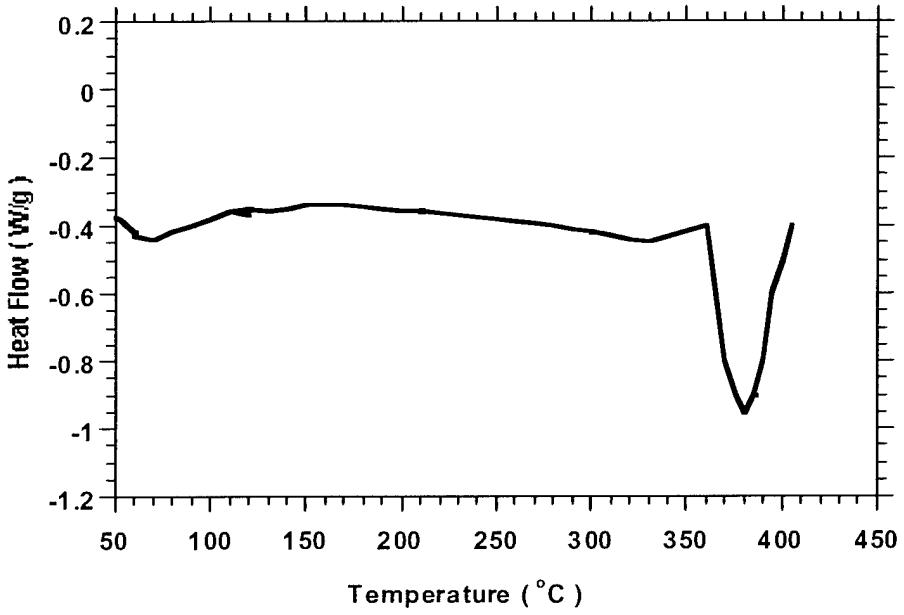


Figure 15 . DSC analysis of 10/90 the PBZT/PEKK molecular composite.

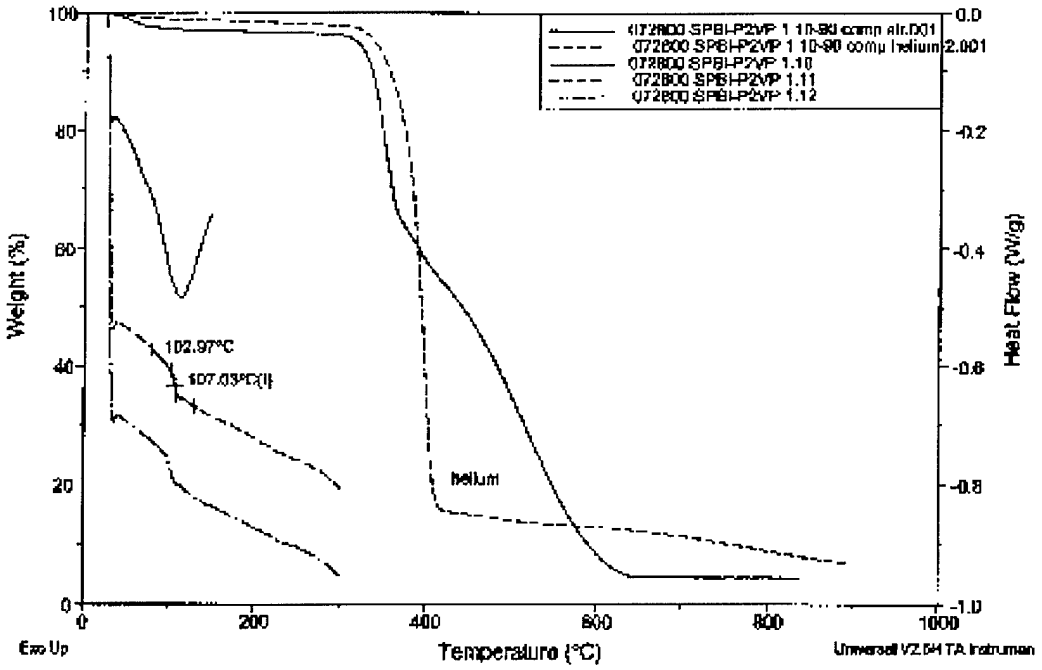


Figure 16. DSC analysis of the P2VP polymer and the SPBI/P2VP molecular composite.

IV.2 Results of Foam Processing

During the first several trials in the processing of PEKK foams, we found that this material tended to produce a cavity in the center. This could be due to the very large constant of thermal expansion (CTE) that resulted in thermal stress during cooling, coupled with the very low viscosity at elevated temperatures. After several trials, however, it was possible to nearly eliminate the cavity completely, as shown in Figure 17.

Figure 17. A representative microcellular PEKK foam.

Microcellular foams were also processed successfully from poly(2-polypyidine)(P2VP) (Figure 18). As the density of the foams was reduced, the color became lighter, as shown going from left to right in Figure 18.

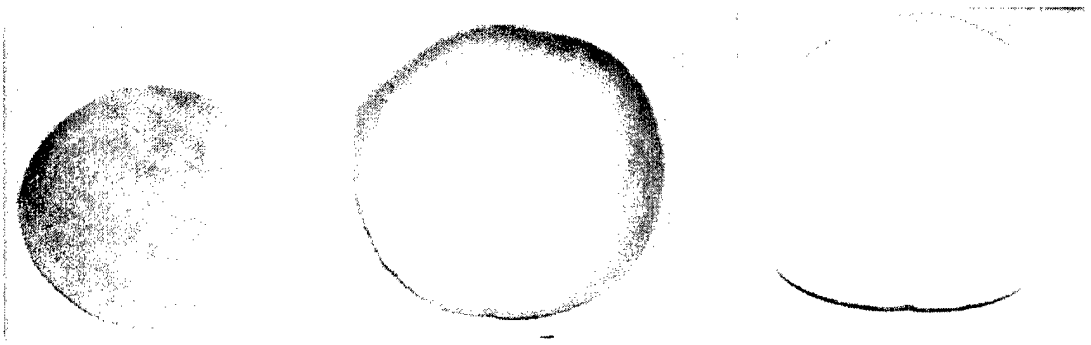


Figure 18. Microcellular foams prepared from poly(2-vinylpyridine)(P2VP).

It has been very difficult to foam the PBZT/PEKK molecular composites. We have tried to foam this material at various temperatures and pressures and obtained only high density foams; see Figure 19 (density ranged from 0.92 to 1.1 g/cc). To increase the "softness" of the molecular composites (MC) at elevated temperatures, we blended the 10/90 MC with various amounts of PEKK powders, and this resulted in foams with lower densities. The concentration of bubbles in the sample increased and the density depended on the processing conditions. A typical foam sample is illustrated in Figure 20.

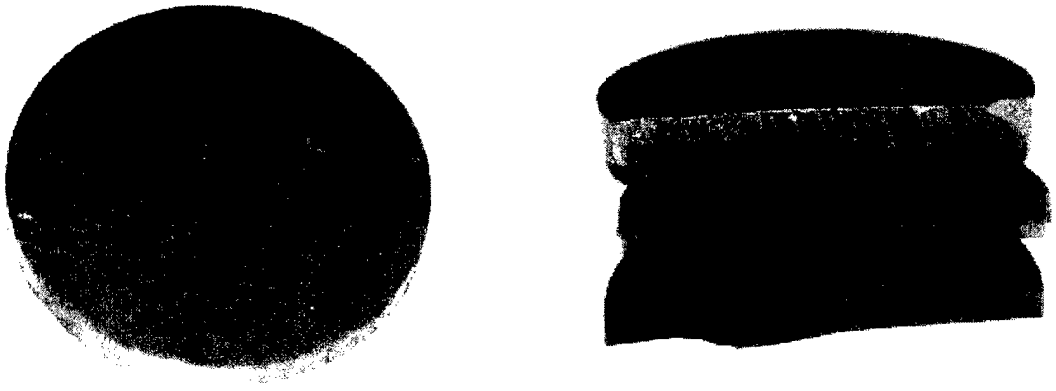


Figure 19. High density foams processed from 10/90% PBZT/PEKK molecular composite.

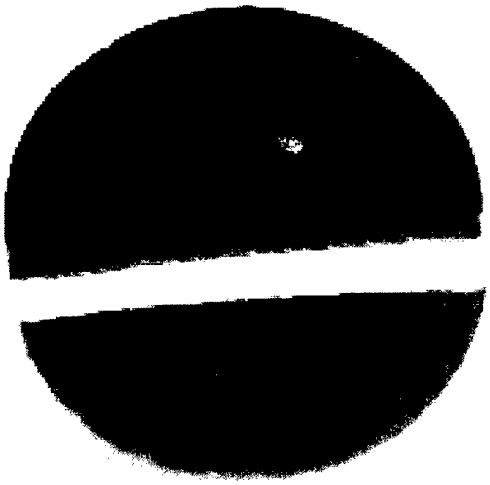


Figure 20. Foam processed from the blend of 50% of 10/90 PBZT/PEKK molecular composite and 50% of PEKK powder.

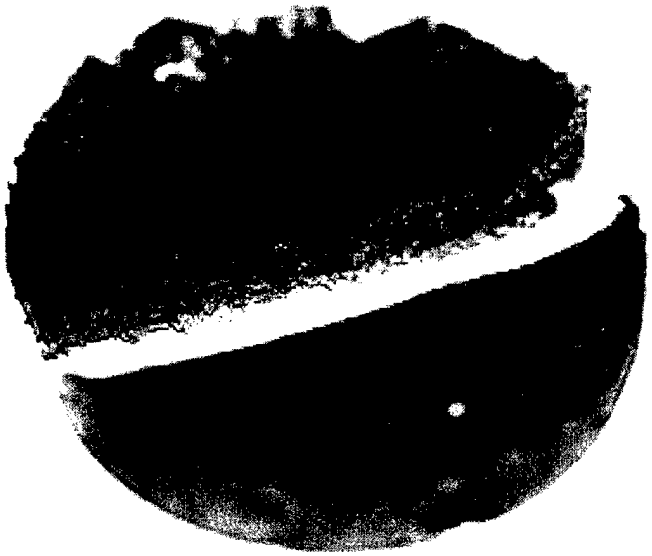


Figure 21. Foam processed from the blend of 10% of PBZT fibers and 90% of PEKK powder.

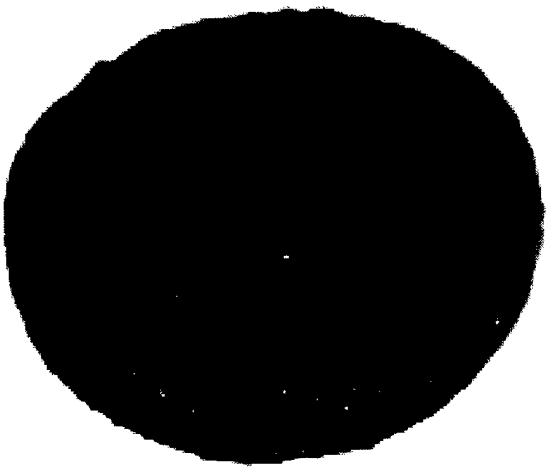


Figure 22. Microcellular foam prepared from 10/90 SPBI/P2VP molecular composite.

We have also blended PBZT fibers with PEKK powders and processed the product into foams. One example that contained 10% of PBZT fibers and 90% by weight of PEKK powders is shown in Figure 21. Among the three different categories of foams mentioned above, this one was easiest to process. Foams with very low densities could be achieved, but they were not molecular composites. Therefore, we did not spend more effort in processing this kind of foam.

After trying for about two years, we still could not reduce the density of the molecular composites lower than 0.7 g/cc. Therefore, we decided to modify our foaming process. A new technique has been developed for the foaming of molecular composites. It turned out that we could reduce the density of PBZT/PEKK molecular composite foams to the value between 0.5 to 0.6 g/cc. SEM photos of these materials will be shown in the next section.

Dr. Arnold synthesized sulfonated SPBI/P2VP molecular composites. Two batches were prepared, one containing 5% and another containing 10% SPBI rigid rods. The batch with 5% SPBI had contamination and could not be consolidated by any means. The other one with 10% SPBI, could be foamed. Thin films cast from the solution were successfully foamed at UC. The SEM results showed that their microstructures were very uniform and the cell size was less than 10 μm. The relative density and cell size could be tailored by varying the foaming conditions. After precipitation, the composite could no longer be dissolved in any solvents. WMR foamed it using the new proprietary foaming technique to give the foam shown in Figure 22. The density of the foams obtained was

about 0.78 g/cc, and this density can be further reduced if desired. The foam was brittle, however, and Dr. Arnold indicated that this MC might crosslink at elevated temperatures. This behavior increased its resistance for foaming. There may be still some contamination in this batch of MC because of its lower degree of consolidation relative to PBZT/PEKK.

IV.3 Results of SEM analyses

SEM results showing morphologies[33-37] of PEKK foams are presented in Figure 23. Their densities were 0.65 and 0.52 g/cc for the top and the bottom figure, respectively. The pore sizes ranged from 10 to 100 μm depending on the processing conditions.

The foams from the blend of 10% PBZT fibers with 90% PEKK powder were processed with conditions chosen to try to reduce the densities. SEM analyses showed that the diameter of the bubbles ranged from 100 to 700 μm.

SEM photomicrographs for the 10/90 PBZT/PEKK molecular composite foams showed that the bubbles were 20 – 60 μm in diameter and the density was quite high (about 1.1 g/cc.); see Figure 24. After many attempts the density was reduced to about 0.92 g/cc (Figure 25).

The morphologies of microcellular poly(2-vinylpyridine)(P2VP) foams by SEM are shown in Figures 26 and 27. The cell size ranged from 50 to 100 μ m.

During the third year of this project we prepared PBZT/PEKK with 5% PBZT. This rod content was lower then the 10 - 30% used in the first two years. The reason for this reduction of rod percentage was to decrease the rigidity of the molecular composite, making it easier to foam. Initial trials using this 5/95% of MC have resulted in microcellular foams with densities about 0.92 g/cc, as compared to 1.1 g/cc that we obtained earlier for the 10/90 MC foam. This density was considered too high, and we therefore tried to further reduce the densities of the MC foams.

After we modified our foaming technique, we were able to reduce the density of the PBZT/PEKK molecular composite foam to about 0.78g/cc (Figure 28). The most recent foams (5/95) processed are shown in Figure 29. The amount of porosity appeared to be quite similar to that of a PEKK foam that we processed before that had a density of 0.52 to 0.65g/cc. The pore size ranged from 10 to 40μm, and the density was in the range 0.5 - 0.6g/cc.

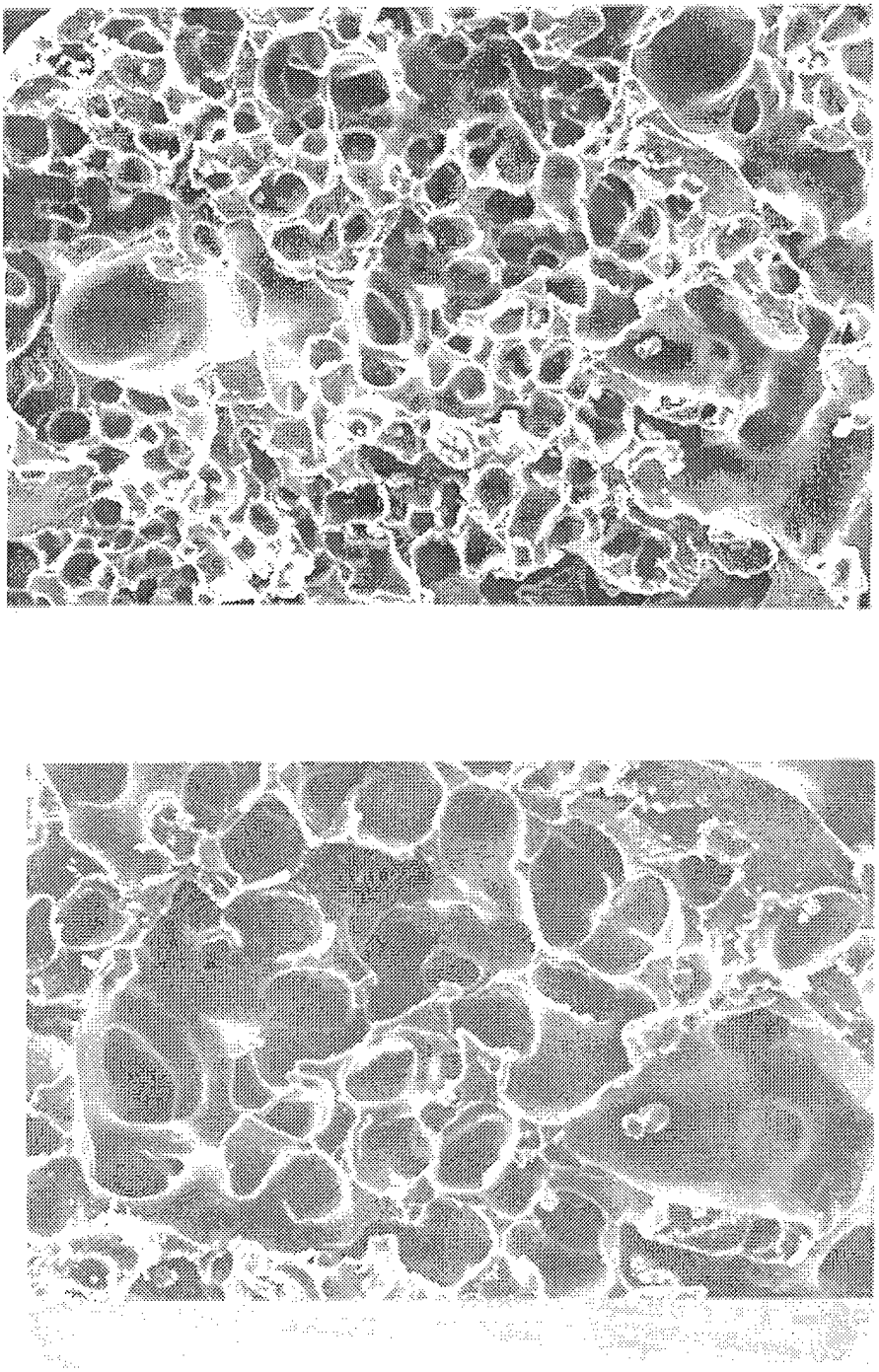


Figure 23 . Microcellular PEKK foams with densities 0.65 g/cc (top) and 0.52 g/cc (bottom).

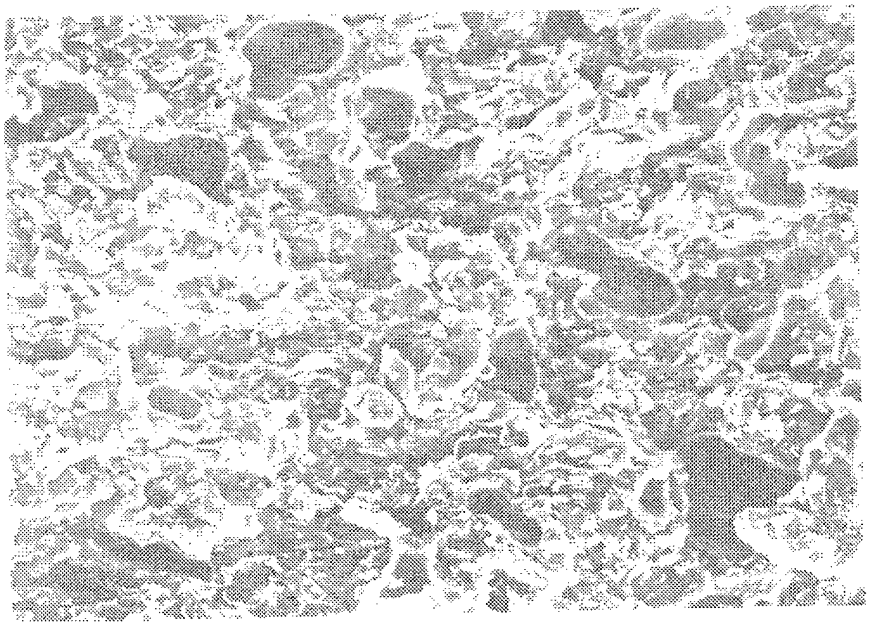


Figure 24. High density 10/90 PBZT/PEKK molecular composite foam (1.1 g/cc).

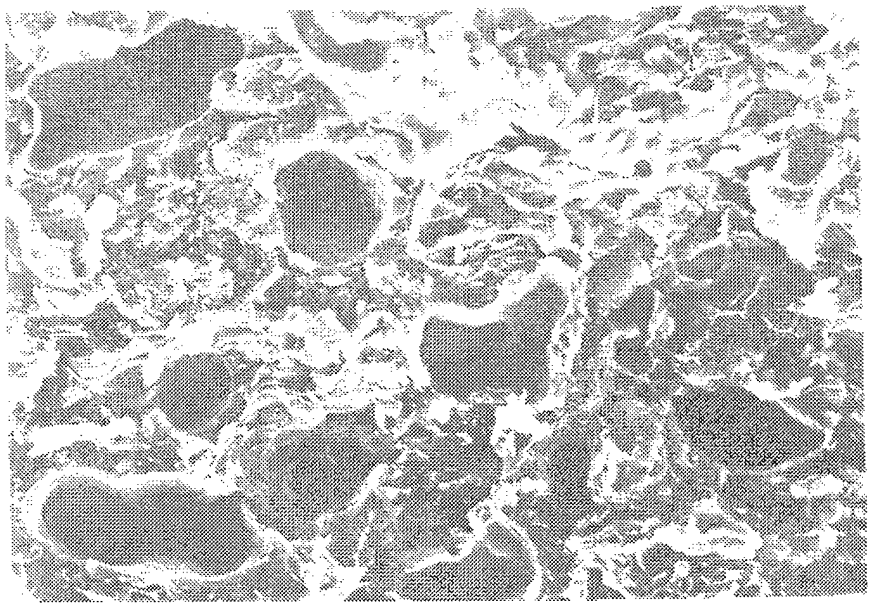


Figure 25. The 10/90 PBZT/PEKK molecular composite foam in which the density was reduced to 0.92 g/cc.

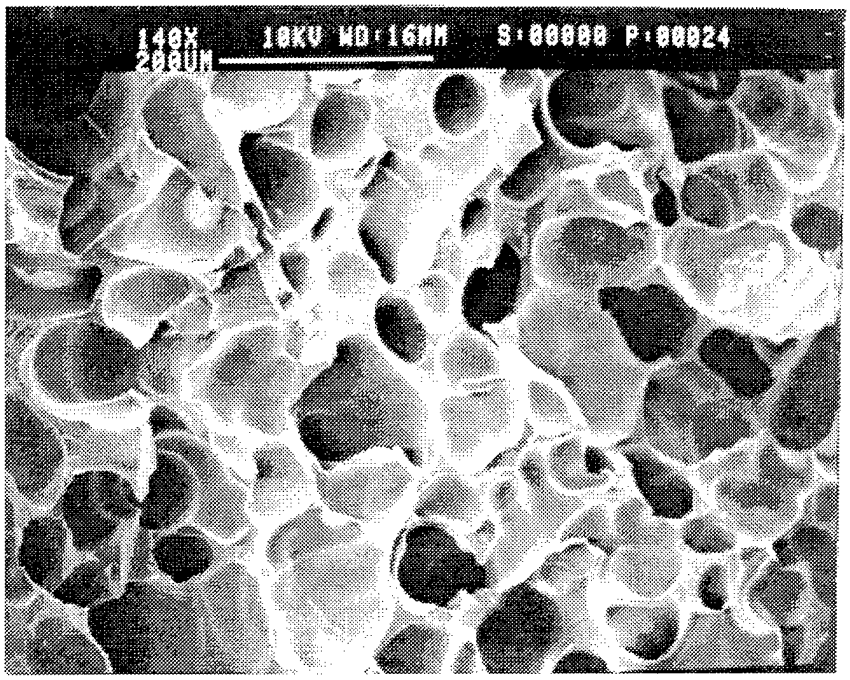


Figure 26. SEM photo of microcellular P2VP foam with intermediate density.

Figure 27. SEM photo of microcellular P2VP foam with low density.

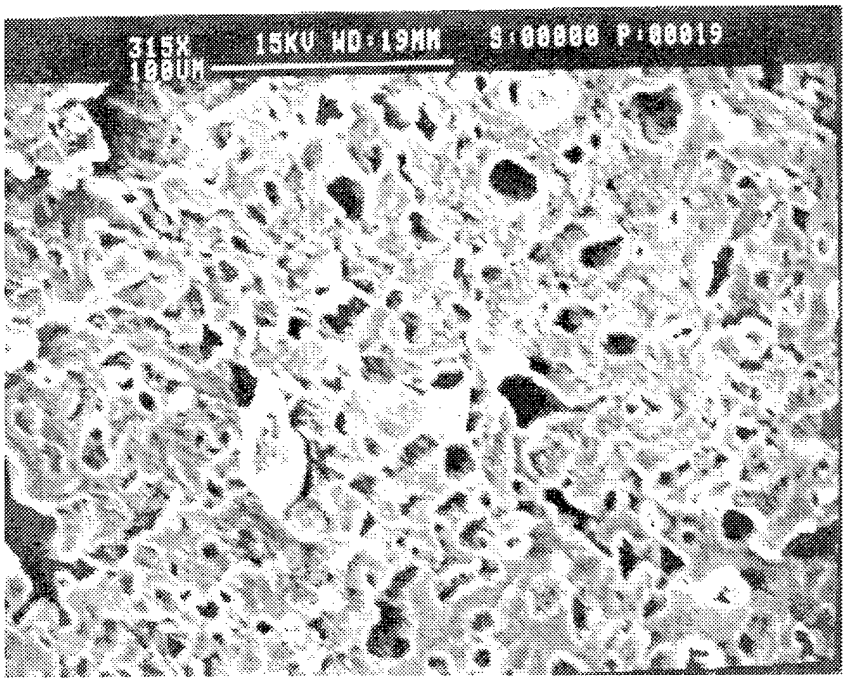


Figure 28. Microcellular PBZT/PEKK molecular composite foam processed by the modified foaming technique.

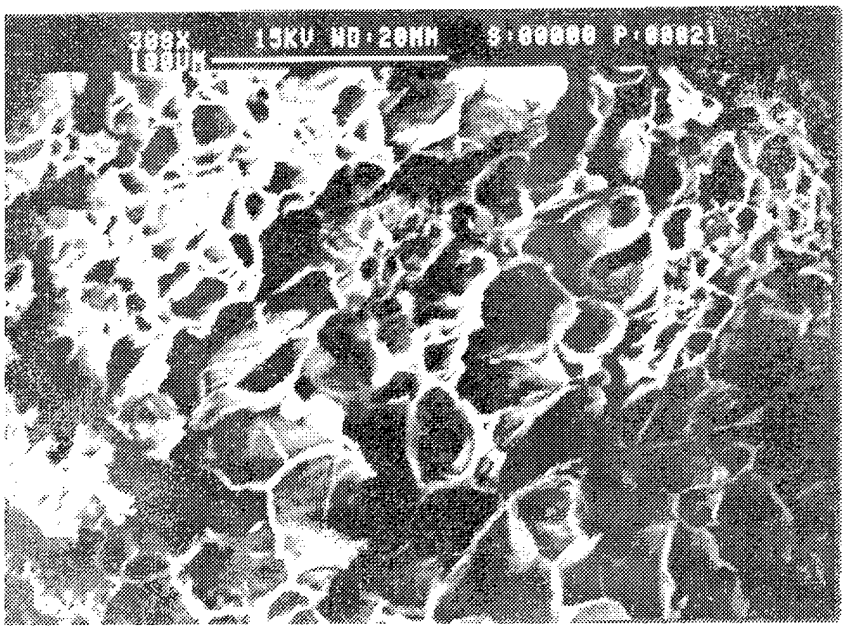


Figure 29. Most recent PBZT/PEKK molecular composite foam, showing that density can be reduced to about 0.5 - 0.6 g/cc.

In the case of the SPBI/P(2VP) molecular composites, foams were prepared from the one containing 10% of SPBI rigid rods. Thin films cast from solution were successfully foamed at UC. The SEM results show that their microstructures were very uniform and the cell size was less than 10 μm. The relative density and cell size could be tailored by varying the foaming conditions. After precipitation, the MC could no longer be dissolved in any solvents, but WMR has foamed it using the modified foaming technique. The density of the foams obtained (Figure 30) is about 0.78 g/cc, and its density can be further reduced if desired. Since this MC was brittle we did not spend more effort in foaming it.

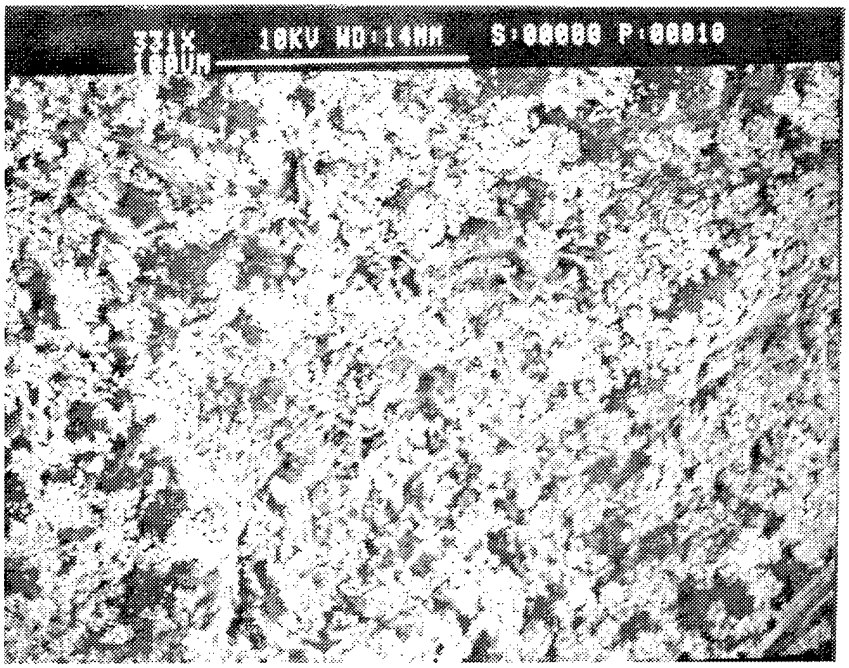


Figure 30. Microcellular foam processed from the SPBI/P2VP molecular composite.

IV.4 Mechanical Properties

Compression tests[38-41] were performed to evaluate the stress-strain relationships of the microcellular foams processed from PEKK, PBZT/PEKK, P2VP, and SPBI/P2VP polymers and some of their molecular composites. The combined results were plotted together to facilitate comparisons.

For comparisons, we plotted specific mechanical properties versus the applied strain, where specific mechanical properties are defined as mechanical properties (such as modulus and strength) divided by the density of the material. Figure 31 shows the specific compression strength of various foams as a function of the applied strain. The results included microcellular foams of PEKK, 10/90 PBZT/PEKK MC, 50% 10/90 PBZT/PEKK MC, blended with 50% PEKK, 10% PBZT fibers blended with 90% PEKK, and a Divinycell HT110. The densities of the PEKK foams were 0.71 and 0.65 g/cc for the upper and the lower curves, respectively. The results indicated that Divinycell HT110 reached a plateau after the applied strain was about 4%. In contrast, the PEKK and molecular composite foams did not have a plateau. The specific compression strength increased as the applied strain was increased. There was no distinct fracture behavior after the foams were loaded to about 76% strain. This showed that our microcellular foams were very "ductile" and had very high fracture toughness.

The material vendor for PEKK did not provide the compression properties, but instead gave the tensile strengths. The specific tensile strength of a solid PEKK sample was 102 MPa/g/cc that was also the yield strength for our PBZT/PEKK molecular composites. The solid PEKK sample has a clean fracture whereas our foams did not show any sign of fracture after they were loaded to 300 MPa/g/cc. Apparently, the large improvement in mechanical behavior was due to the unique morphology of the foam. The specific compression modulus is plotted as a function of the applied strain in Figure 32. The results, similar to the specific compression strength, were significantly higher than that of Divinycell. At 10% strain, the values of PEKK foams were about 2.5 times higher than that of Divinycell, whereas the values of PBZT/PEKK were about 5 times higher than that of Divinycell. It should be noted that the specific modulus was normally calculated at a point or several points rather than for the entire stress-strain curves. The numerical comparisons of the specific compression strength and modulus are listed in Tables 1 and 2 at 10% and 30% strain, respectively.

The compression stress-strain relationships of 10/90 SPBI/P2VP are illustrated in Figure 33. This molecular composite started to lose its load carrying capability after it reached about 16% strain. Fracture occured at about 32~42% strain. Although this material was not brittle relative to other polymers, it was considered brittle among all the microcellular foams that WMR processed. Also Dr. Arnold indicated this material crosslinked at elevated temperatures. We felt that this batch of SPBI/P2VP might have a small amount of contamination because it did not consolidate as well as the other molecular composites that we processed.

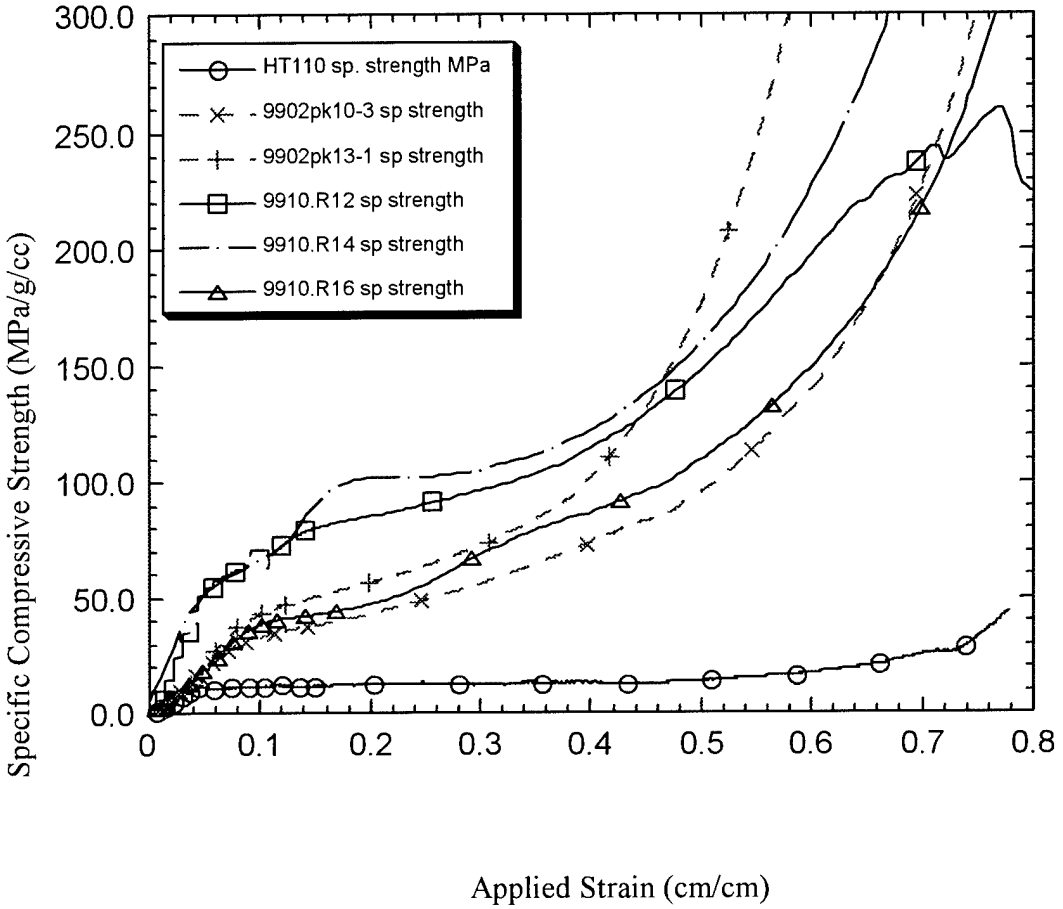


Figure 31. Comparison of specific compression strength for PEKK, PBZT/PEKK MC and a Divinycell foam.
HT 110: Divinycell; 9902pk10-3 and 9902pk13-1: PEKK foams;
9910R12: 10/90 PBZT/PEKK MC foam;
9910R14: 50% 10/90 PBZT/PEKK and 50% PEKK blend foam;
9910R16: 10% PBZT fiber and 90% PEKK blend foam.

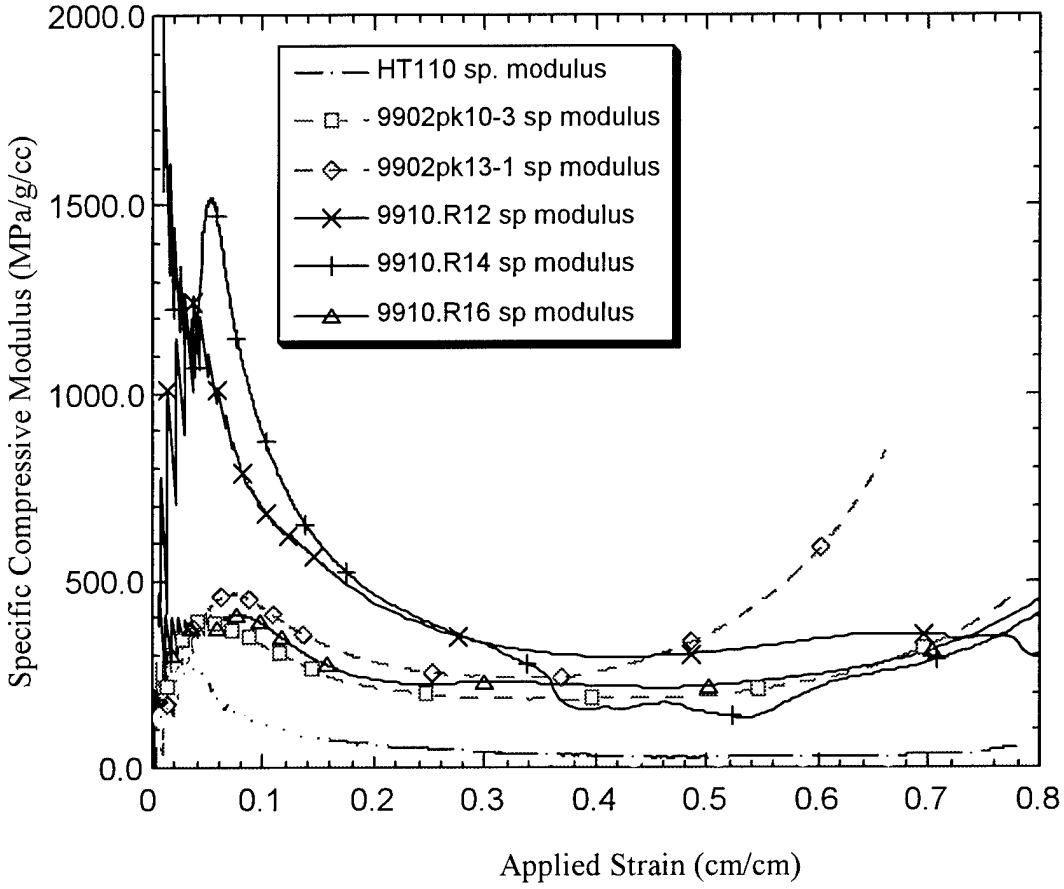


Figure 32.Comparison of specific compression modulus of PEKK, PBZT/PEKK MC, and a Divinycell foam.

HT 110: Divinycell; 9902pk10-3 and 9902pk13-1: PEKK foams;

9910R12: 10/90 PBZT/PEKK MC foam;

9910R14: 50% 10/90 PBZT/PEKK and 50% PEKK blend foam;

9910R16: 10% PBZT fiber and 90% PEKK blend foam.

Table 1. Comparisons of specific mechanical properties of PEKK, PBZT/PEKK MC, and Divinycell foams at 10% applied strain.

	Divinycell	PEKK foams	10%PBZT/PEKK MC foam	50% 10/90 PBZT/PEKK MC and 50% PEKK foam	10%PBZT fibers and 90% PEKK foam
Specific Modulus (MPa/Relative Density)	117.2	375.7	688.5	892.5	384.1
Specific Compression Strength (MPa/Relative Density)	11.7	37.6	66.5	89.1	38.3

Table 2. Comparisons of specific mechanical properties of PEKK, PBZT/PEKK MC, and Divinycell foams at 30% applied strain.

	Divinycell	PEKK foam	10%PBZT/PEKK MC foam	50% 10/90 PBZT/PEKK MC and 50% PEKK foam	10%PBZT fibers and 90% PEKK foam
Specific Modulus (MPa/Relative Density)	40.7	214.2	333.3	329.1	229.1
Specific Compression Strength (MPa/Relative Density)	12.2	64.3	96.4	98.8	68.6

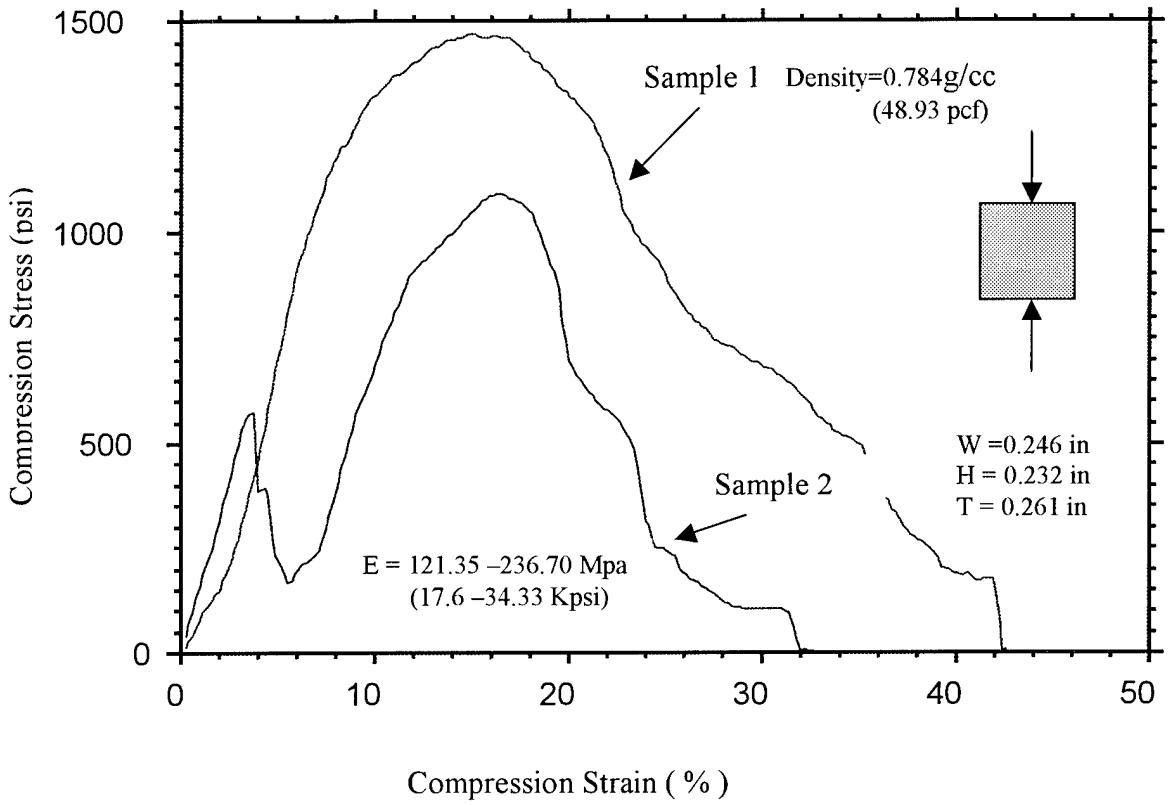


Figure 33. Compression stress-strain relationships of SPBI/P2VP MC foams.

The compression stress-strain relationships of a high density 5/95 PBZT/PEKK MC foams are plotted in Figure 34. The yield strength was between 9 and 10 kpsi. After the applied strain reached 15 to 20% the stress-strain curves dropped but they recovered at a higher strain level. Numerical comparisons are listed in Table 3.

The sample processed by our modified foaming technique was too small for mechanical testing. The foam morphology, however, indicated that its density was about 0.5 to 0.6 g/cc. We tried to use the modified technique to foam PARMAX, and did successfully reduce the density to 0.49 g/cc. A compression test showed that this foam had an initial modulus as high as 129 MPa (18.8 kpsi). The compression stress-strain curve revealed that its modulus increased as the applied strain was increased. This behavior continued until the applied load reached 33 kpsi at a strain of 78%.

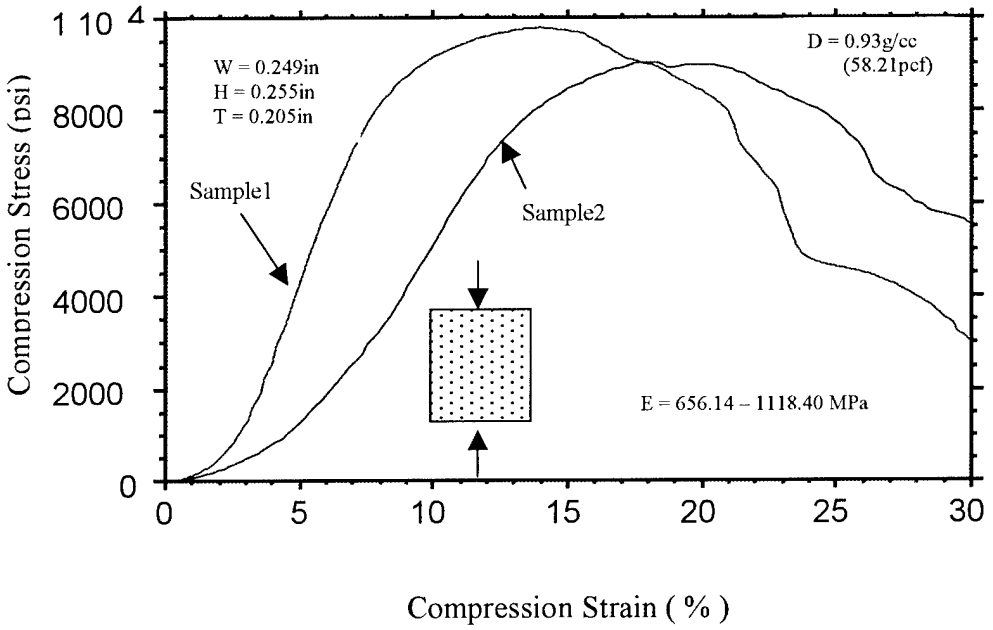


Figure 34. The stress-strain relationship of PBZT/PEKK (5/95%)MC foams.

Table 3.Comparisons of specific mechanical properties of various foams at 10% applied strain.

	Divinycell	PEKK foam	10%PBZT/PEKK MC foam	50% 10/90 PBZT/PEKK MC and 50% PEKK foam	5/95 of PBZT/PEKK MC foam
Specific Modulus (MPa/Relative Density)	117.2	375.7	688.5	892.5	954
Specific Compression Strength (MPa/Relative Density)	11.7	37.6	66.5	89.1	70-75

V. Microcellular Foams From Some Other Polymer Matrices And Molecular Composites

V 1. Microcellular Foams From Some Other Polymer Matrices

In addition to the PEKK and PBZT/PEEK foams prepared by WMR, some other polymer matrices, such as polysulfone(PSF), poly(ethersulfone)(PESF),poly (phenylsulfone)(PPSF), poly(etherimide)(PEI), and poly(etherketoneketone)(PEKK) have also been successfully foamed at UC using the two-stage batch foaming process originally developed at MIT. In this foaming process, the first stage involves saturation of the polymer with non-reactive gas, such as CO_2, with the second stage corresponding to the inducement of a thermal instability in the gas-saturated polymer sample to cause bubble nucleation and growth. Some typical SEM micrographs of the microcellular foams are shown in Figure 35. In all of these foams, except that from PEKK, the cell size was smaller than 10μm and the cell density was on the order of 10^{11}cells/cm^3. From the SEM micrographs, one can also see that under the same foaming conditions, the cell sizes of the PPSF and PEI foams were much smaller then those of the PSF and PESF foams. This is mainly because the stiffness of the PPSF and PEI chains. For PEKK, the middle portions of the sample were not foamed because PEKK is a semicrystalline polymer and it is very difficult for CO_2 to diffuse into the polymer matrix even after a long time (120 hours) to form a uniform polymer/gas solution. The CO_2 content in PEKK was only 2.4% and had a gradient which decreased from the edge to the center and this caused the size distribution to have a gradient at wall. By carefully choosing the process parameters, some structural aspects of the microcellular foam were successfully controlled. The effects of process parameters on the microstructure and relative density of the foams were studied. Figure 36 showed the effect of foaming temperature on the relative density of the PSF foams. With increase in temperature, the relative density decreased to a minimum of about 0.28 at approximately 185 °C and then began to increase markedly. This is because the mobility of the polymer chains increased greatly at high temperature, so above T_g CO_2 diffused out of the polymer matrix instead of supporting cell nucleation and growth. As a result, the cells coalesced and the foam structure collapsed, thus increasing density. The average cell size increased linearly with the foaming temperature, as shown in Figure 37. When the temperature was increased, the polymer viscosity decreased, allowing the cells to grow larger. Figure 38 shows that cell nucleation density decreased slightly with increased temperature. Therefore the microstructures of the foams could be controlled by carefully choosing the foaming conditions. Since these materials were prepared for possible use as structural materials, tensile tests were carried out on PSF

foams to investigate the dependences of these properties on relative densities. The results indicated that as the relative density decreased, the tensile strength, modulus, and elongation decreased. Figures 39 and 40 show the relative strength and modulus as a function of foam relative density. The results showed that relative tensile strength was directly proportional to the relative density and the relative modulus was proportional to the square of the relative density. These results are in very good agreement with the theoretical model suggested by Gibson and Ashby[42]. In order to investigate the compression properties of the microcellular foams, we also attempted to prepare larger and thicker foam samples, but it took an extremely long time for CO_2 to diffuse uniformly into the bulk section of a thick polymer sample. If the saturation temperature and pressure could be increased, it would be possible to make larger foam samples.

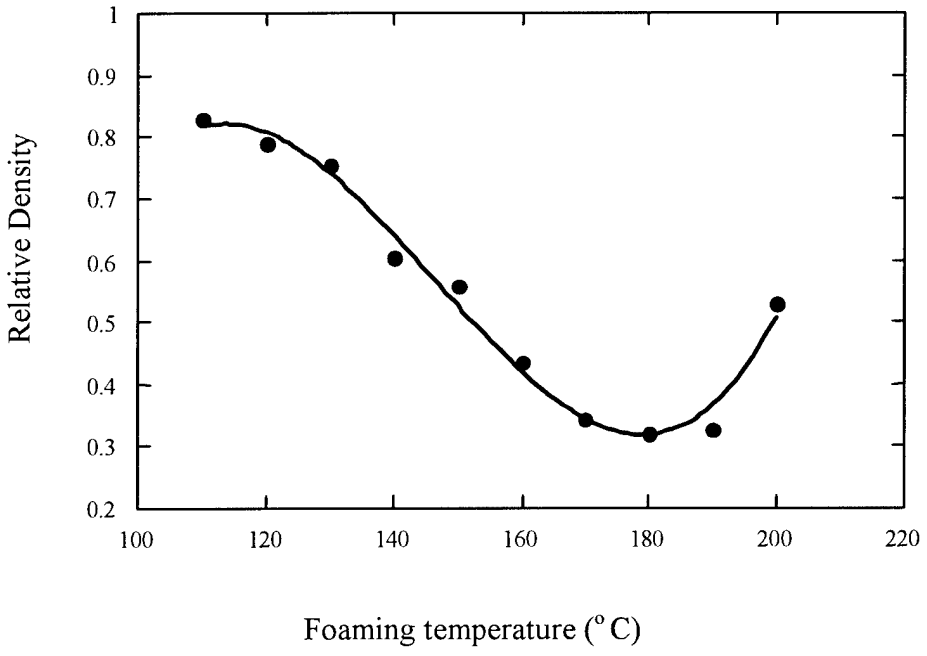
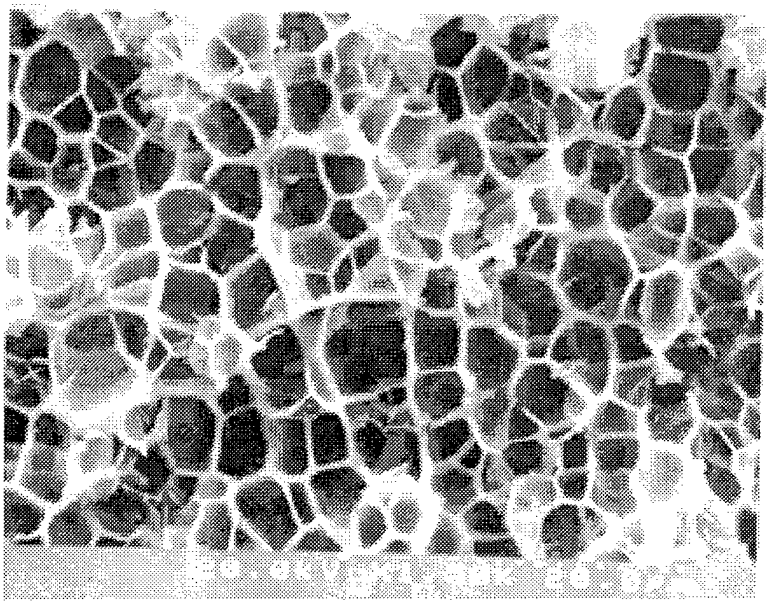
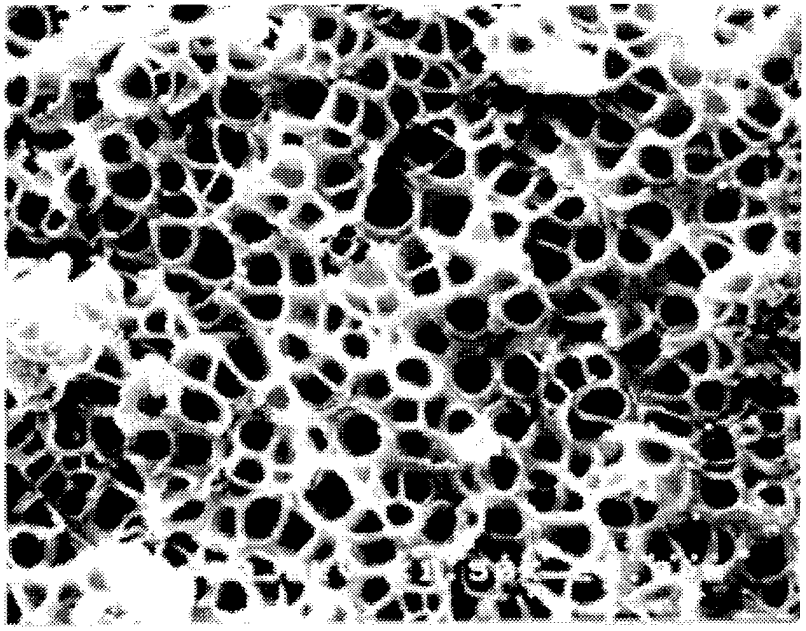


Figure 36. Relative density of PSF foam as a function of foaming temperature.



A



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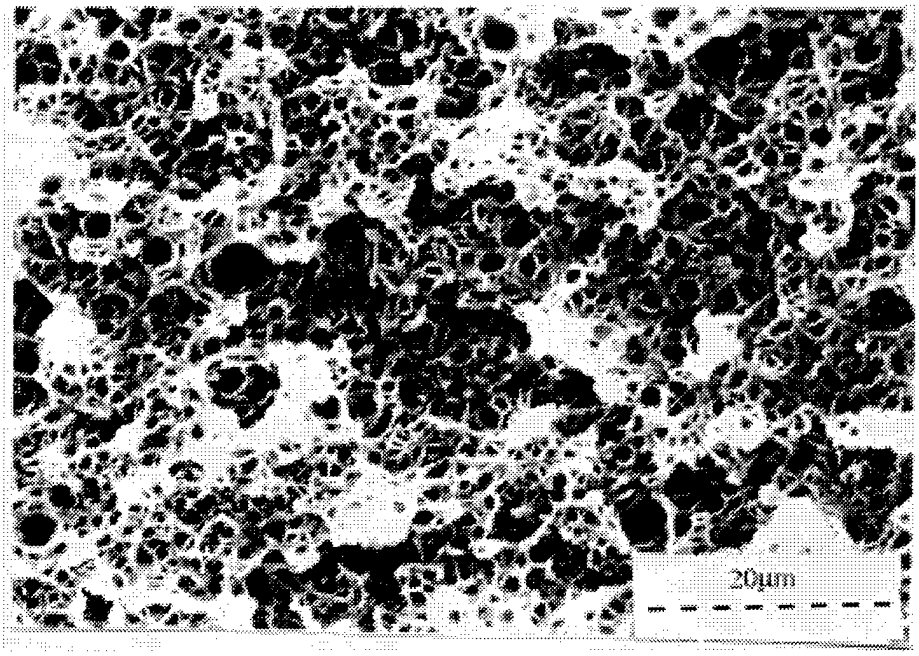
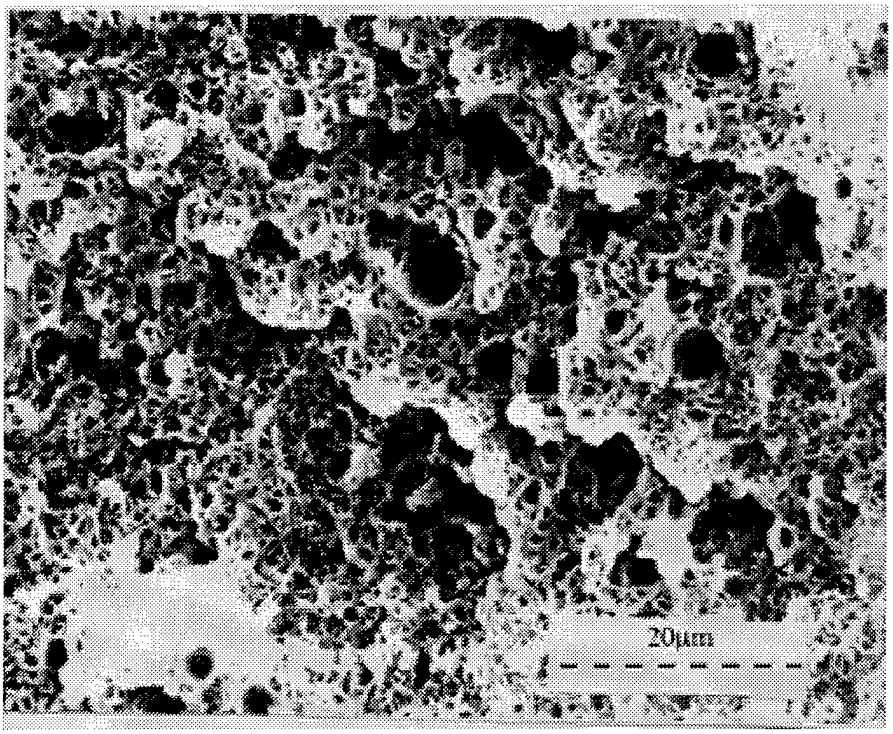
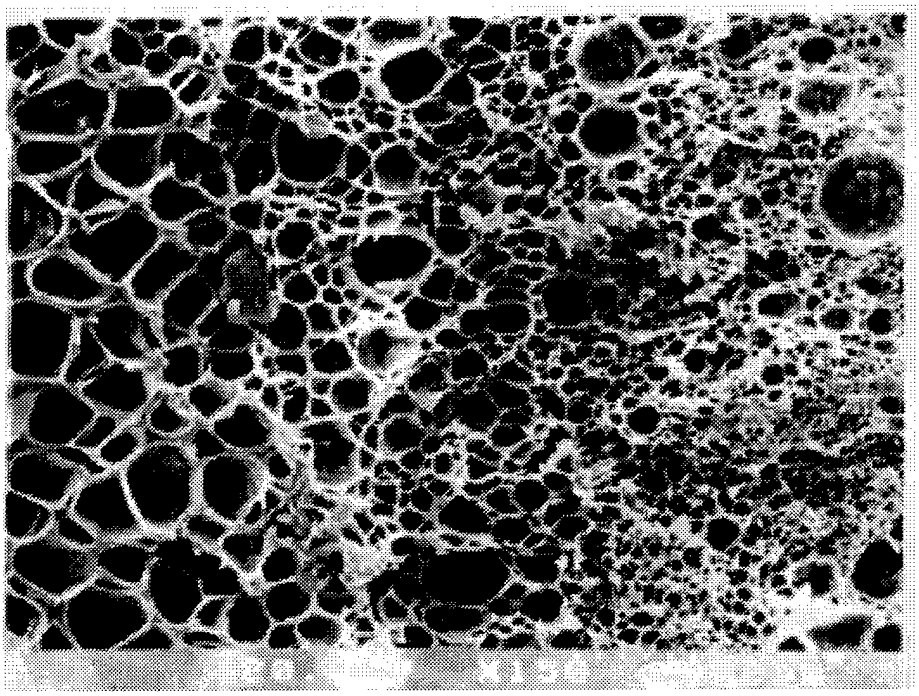


C

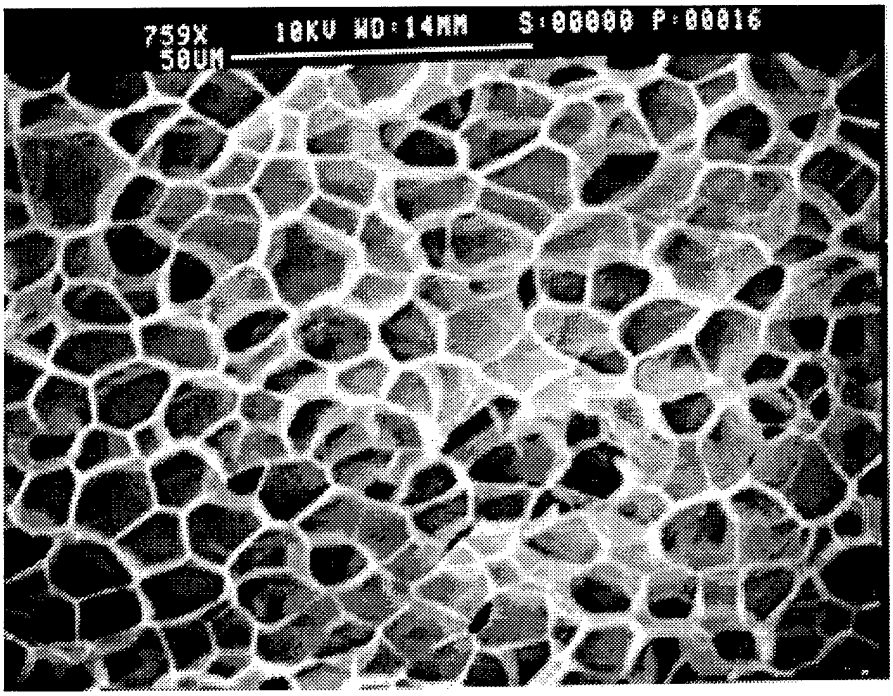


D

E-1



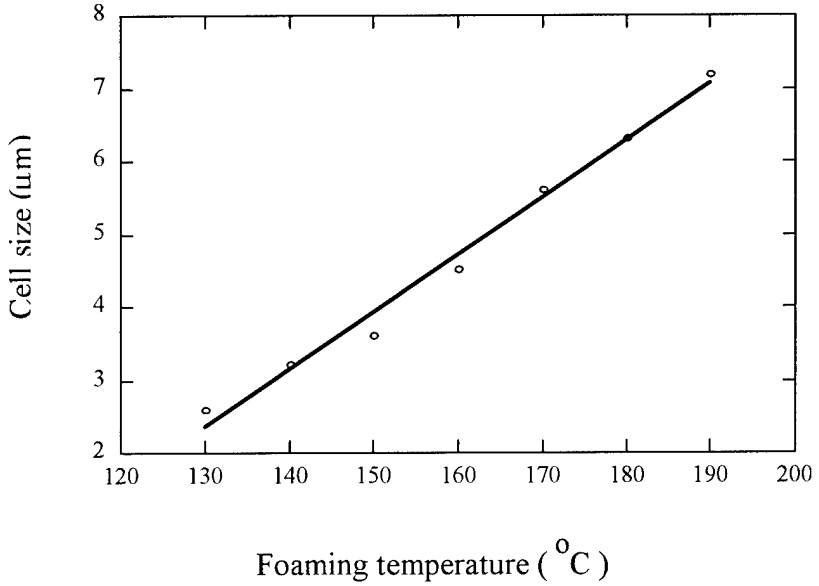
E-2



F

Figure 35. Typical SEM micrographs for the microcellular foams.

A, polysulfone; B, poly(ethersulfone); C, poly(phenylsulfone); D, poly(etherimide). Foaming conditions: CO_2 concentration 9% by weight, foaming temperature: 175°C, foaming time: 30 seconds.
E, poly(etherketoneketone): CO_2 concentration 2.4%
F, poly(2-vinylpyridine): CO_2 concentration 8%, foaming temperature 105 °C.



Figugure 37. Average cell size of PSF foam as a function of foaming temperature.

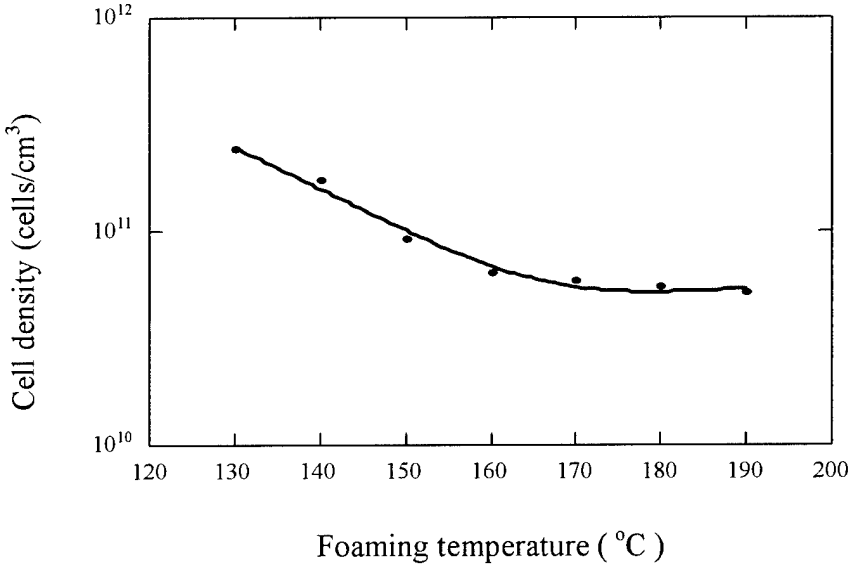


Figure 38. Cell density of PSF foam as a function of foaming temperature.

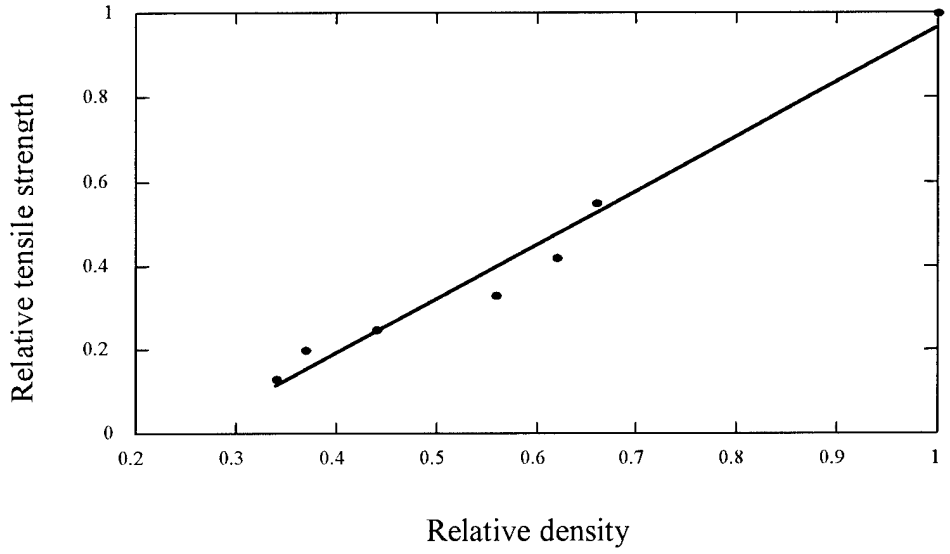


Figure 39. Relative tensile strength fo PSF foam as a function of relative density.

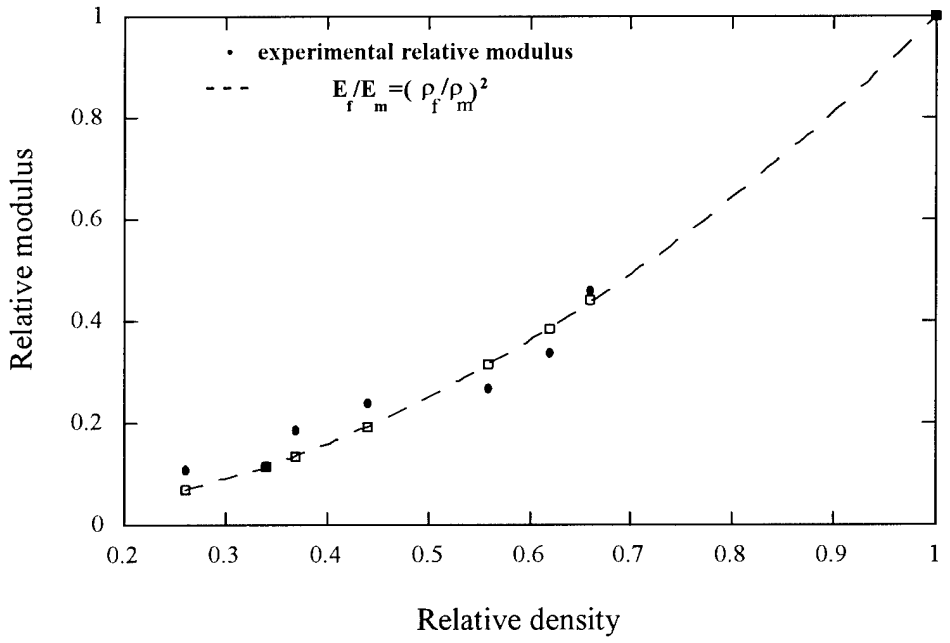
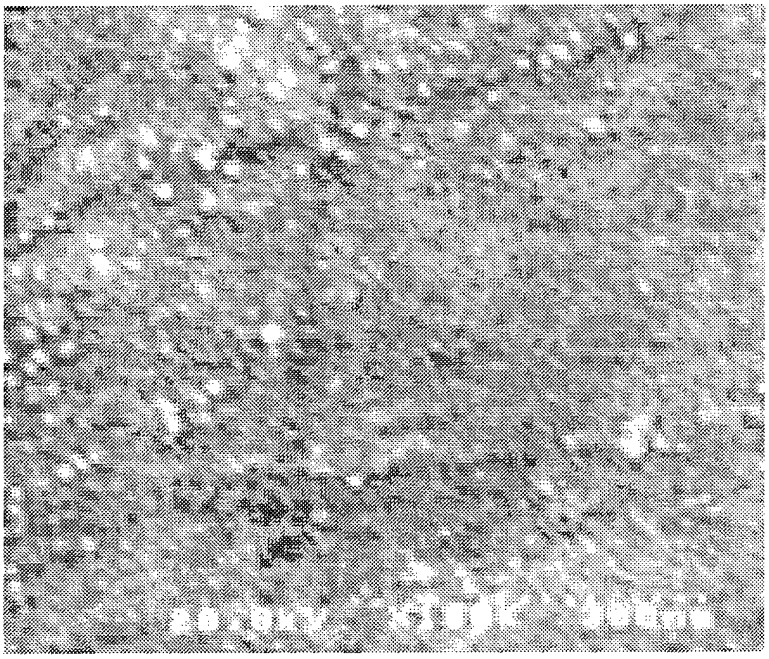


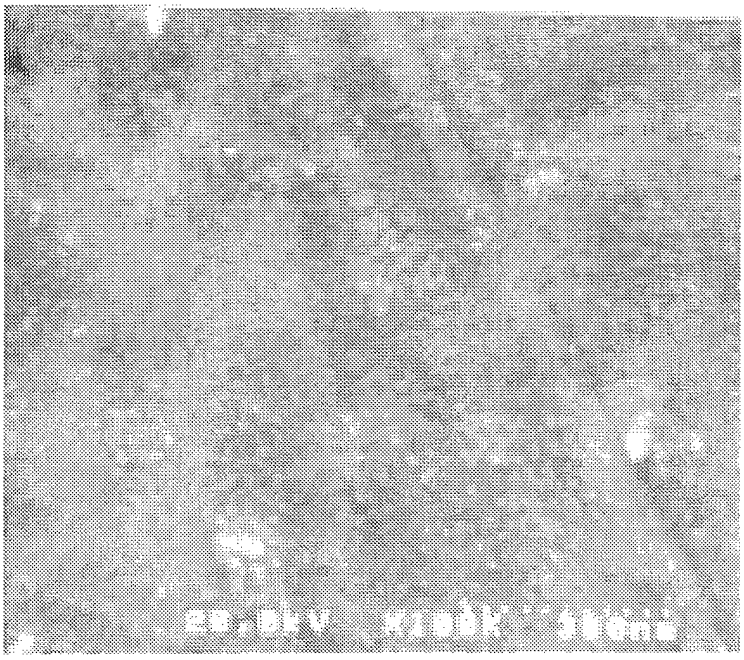
Figure 40. Relative modulus of PSF foam as a function of relative density.

V. 2 Molecular Composites Based Functionalized PSF and PBI

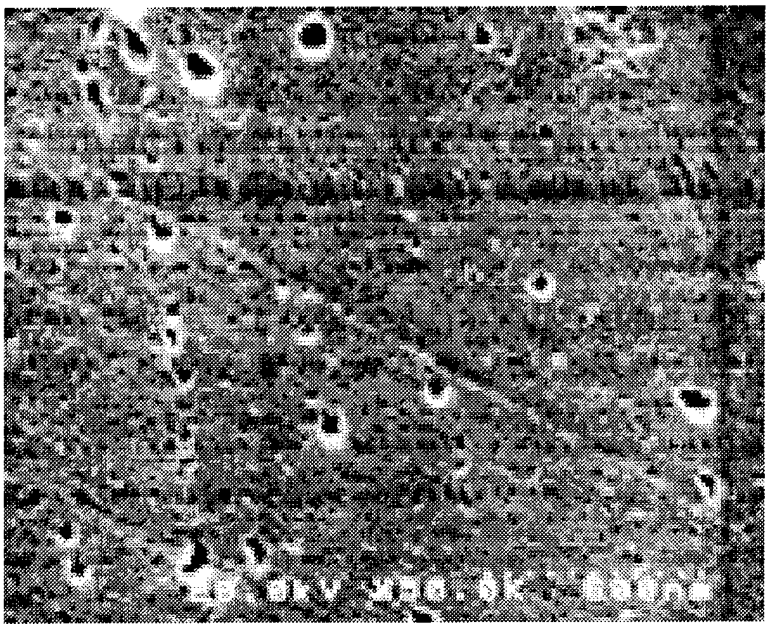
As mentioned above, because the entropy of mixing of polymers is very small and the rigid- rod molecules have strong tendency to segregate, the molecular composite system is not in a thermodynamically miscible state and phase separation occurs readily. An effective method to overcome this problem is to induce specific interactions (such as ion-ion, ion-dipole and acid-base) and thus enhance the miscibility between the two polymers. Recently Dr. Arnold made a molecular composite from poly[(1,7-dihydrobenzo[1,2-d:4,5-d]diimidazole-2,6-diyl)-2-(sulfo-p-phenylene] (SPBI) and poly(vinylpyridine) (PVP) based on the acid-base interaction. The chemistry of this molecular composite is illustrated in Figure 4. Based on this idea we tried to prepare molecular composites from our host polymer matrix polysulfone (PSF) and polybenzimidazole (PBI) (Celazole, Hoechst Celanese). PBI is a high-performance thermoplastic, and has very high glass transition temperature ($T_g = 420\,^{\circ}C$). PBI possesses both donor and acceptor hydrogen-bonding sites which are capable of participating in the specific interactions. Initially, PSF and PBI is an immiscible polymer pair, but introduction of functional groups [such as sulfonate groups (S), or amine groups (N)] into the PSF or PBI resulted in miscible polymer blends. In fact, the SPSF/PBI pair was found to be miscible over the entire composition range when the degree of sulfonation of PSF was higher then 0.5. Clear transparent films were successfully made from the SPSF/PBI molecular composite using a solution casting method. Figure 41 shows the SEM micrographs of the SPSF/PBI films. No phase separation was observed on the nano-scale level. The enhanced miscibility between the SPSF and PBI was mainly due to the ionic interchange between the sulfonic group of the SPSF and the basic sites of the PBI, as illustrated in Figure 42. One very interesting phenomenon is that when the content of PBI exceeded 40wt%, the clear films had nanosized holes (about 30 nm), as shown in the SEM. Because of the nanosize holes in the molecular composites thin films, This kind of material should have potential application as an ultra-membrane. Other polymer pairs, such as NPSF/PBI, NPSF/SPBI, were at least partially miscible, and the enhanced miscibility was due to specific interactions between the two types of polymer chains. SEM shows that there is no phase separation in these molecular composites at the nanoscale level. Figure 43 is the SEM micrograph of 90/10 (w/w) composition of NPSF/SPBI molecular composites. The thermal stabilities and mechanical properties of these molecular composites are under investigation.



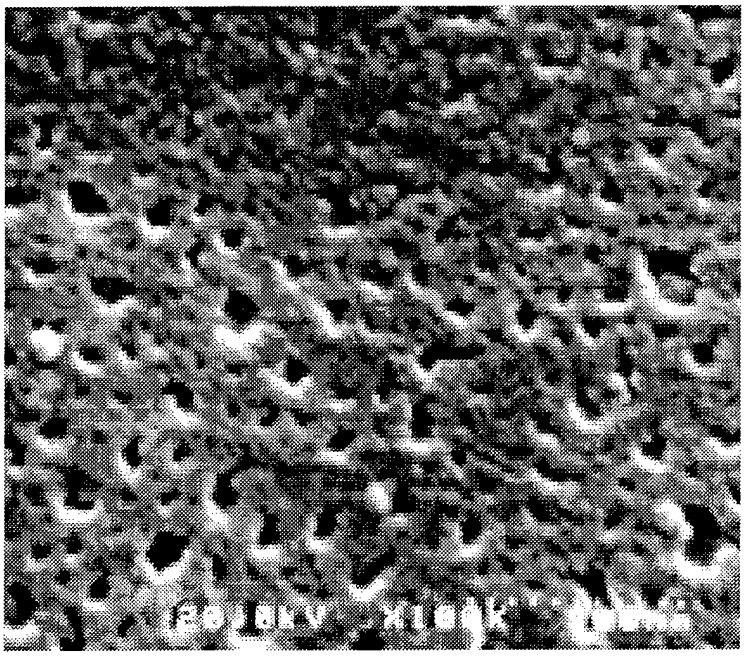
90/10 w/w



80/20 w/w



50/50 w/w



33.3/66.7 w/w

Figure 41. SEM micrographs of SPSF/PBI molecular composite films.

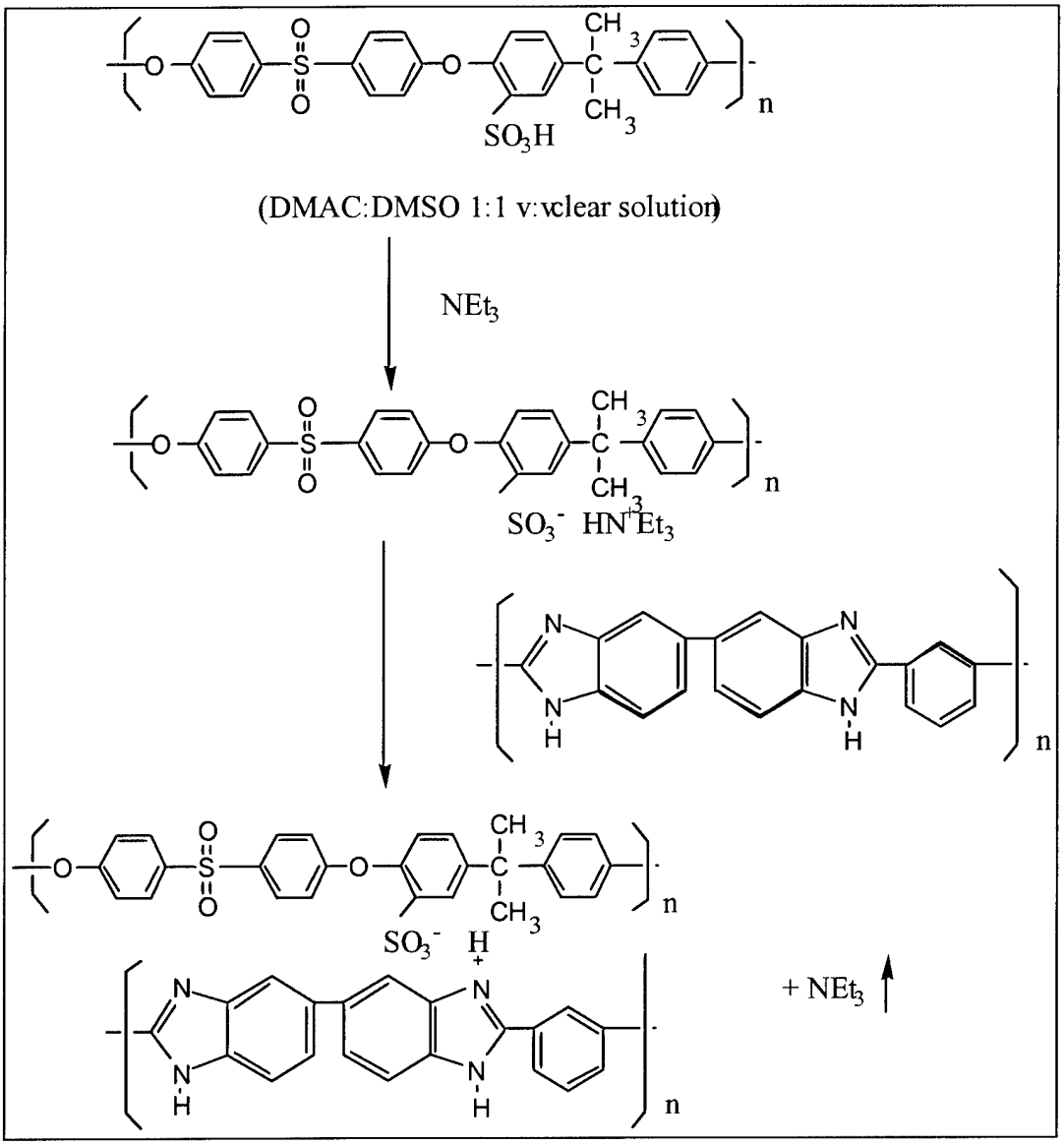
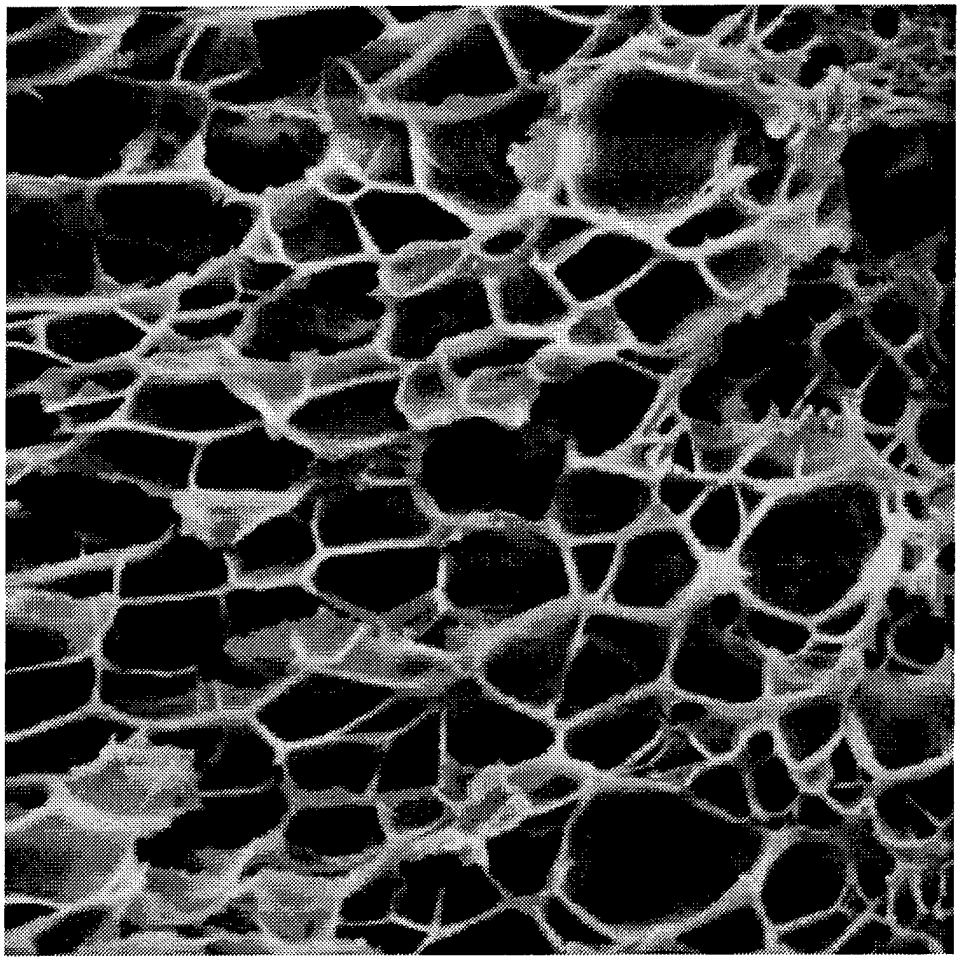


Figure 42 . SPSF/PBI molecular composite formation via ionic interaction.

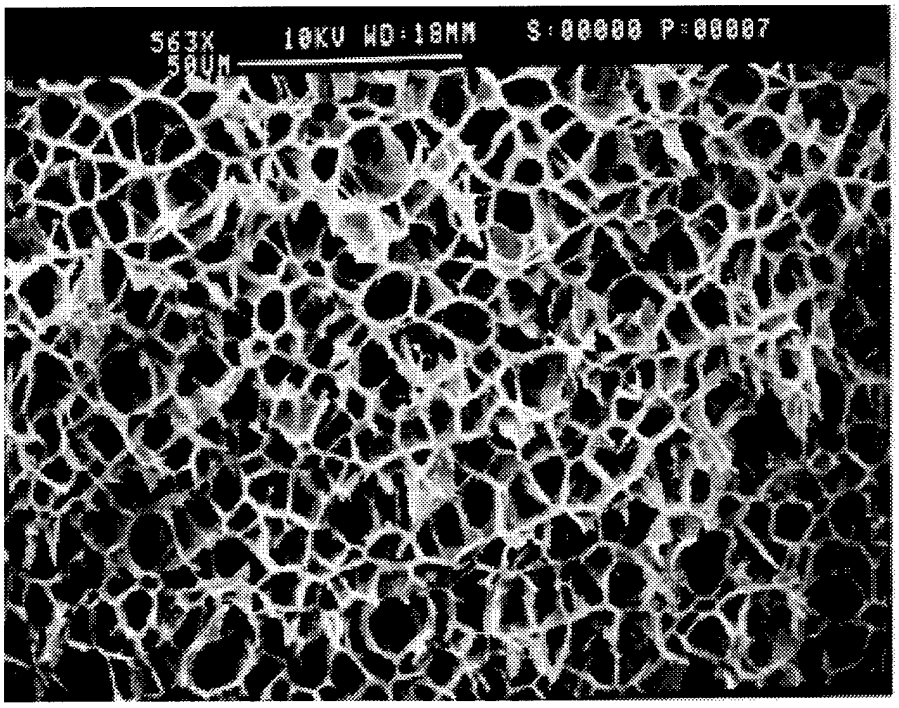
Figure 43. SEM micrograph of the NPSF/SPBI (90/10 w/w) molecular composite.

V.3 Microcellular Foams From Molecular Composites

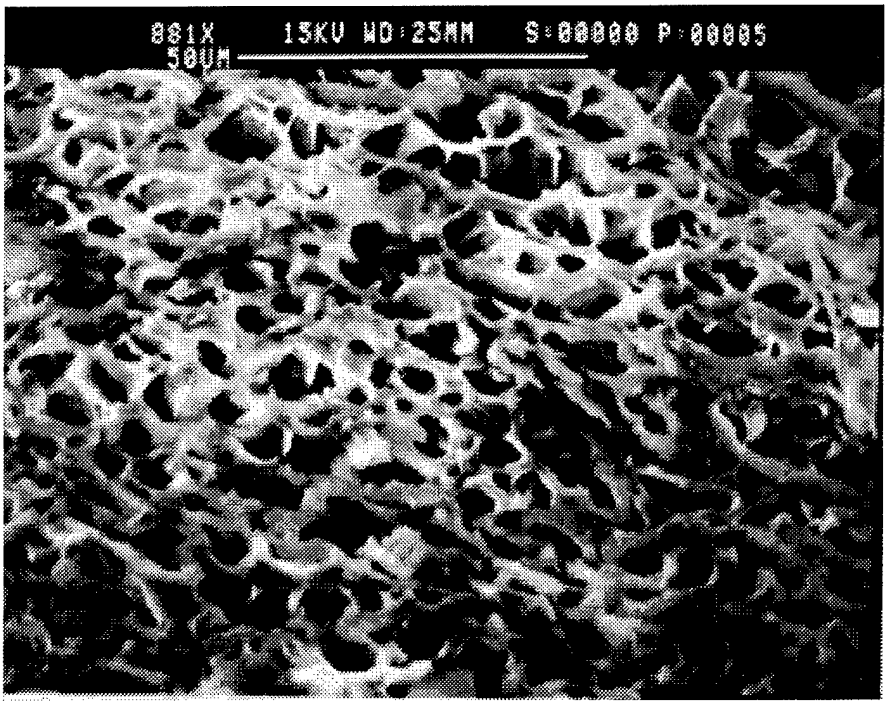
Transparent molecular composite films were prepared using the solution casting method and were dried in a vacuum oven at about 200 °C for at least 10 hours. These thin films (about 0.2 mm in thickness) were successfully foamed using the same method as for the host polymer matrices. Because these films are very thin, the saturation time was only about 24 hours, and the CO_2 content for all these samples was about 7 - 8%. The foaming temperature used was lower and foaming time less than that used for polymer matrices. Some of the SEM micrographs are shown in Figure. 44. Because of the small size and brittleness of these foamed thin films, it was very difficult perform any mechanical test on them.



PEI/PBI 90/10 (w/w)

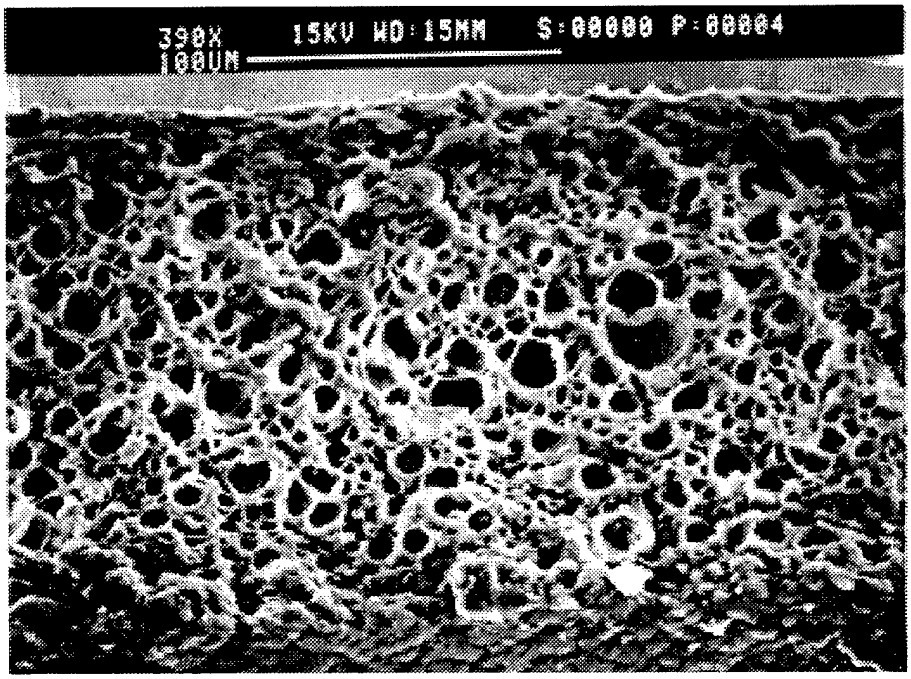


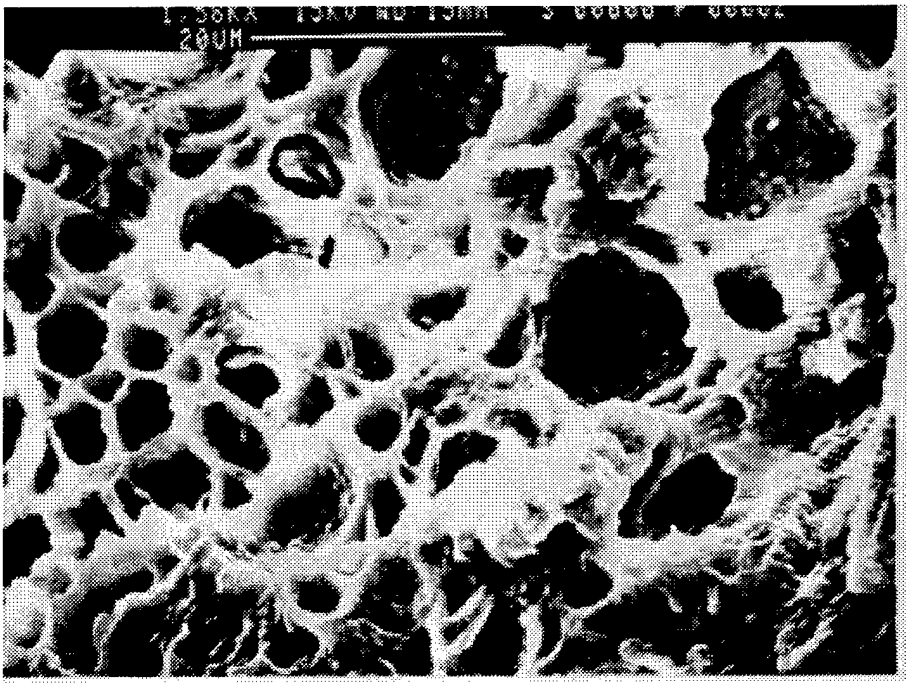
95/5 w/w



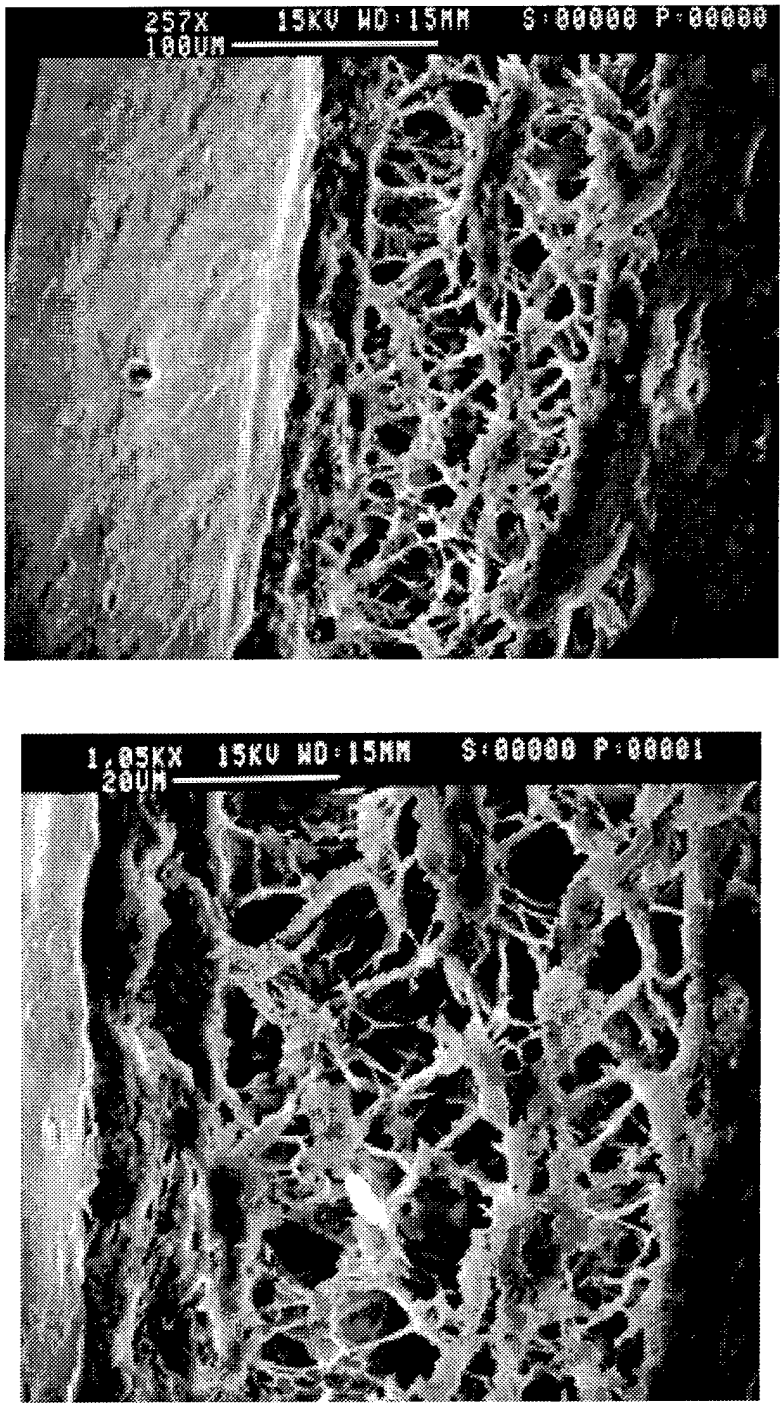
90/10 w/w

P2VP/SPBI





NPSF/SPBI 90/10 (w/w)



NPSF/PBI 90/10 (w/w)

Figure 44. SEM micrographs of the microcellular foams made from the molecular composite thin films.

SUMMARY AND CONCLUSIONS

A number of conclusions can be drawn from this research effort:

(1) The specific modulus of 5/95 PBZT/PEKK MC foam at 10% strain is 2.5 times that of the PEKK foam.

(2) The specific compression strength of 5/95 PBZT/PEKK MC foam at 10% strain is 1.9 times that of the PEKK foam.

(3) The specific modulus of 5/95 PBZT/PEKK MC foam at 10% strain is 8.2 times that of the Divinycell foam.

(4) The specific compression strength of 5/95 PBZT/PEKK MC foam at 10% strain is 6.2 times that of the Divinycel foam

(5) The foam density of the molecular composites was decreased from 1.1 to 0.92 g/cc during the first two years, and to about 0.5 ~ 0.6 in the third year.

(6) The density of the MC foam can be made lower than 0.49 g/cc, as was shown by our trial with PARMAX using WMR's new modified foaming technique.

(7) WMR will file a patent application for our new modified foaming technique.

Large samples of MC foams are needed for aerospace applications and it is important to further reduce their densities. More research efforts are needed in this area.

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GENERAL INFORMATION ON THE GRANT

PI's and Co-PI's:
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Graduate students (part time) supported during the total grant period
J. Braun
G. Rajan
H. Sun
Y. Vu
R. Venkitachalam
R. Zhang
M. Hassan
C. Kumudinie
R. Patil
B. Vu

PUBLICATIONS DURING THE TOTAL GRANT PERIOD

1. H. Sun and J. E. Mark "*Preparation and Mechanical Properties of Microcellular Polysulfone Foams*" Presented at the 4th National Graduate Research Polymer Conference, American Chemical Society, Hattiesburg, MS, June 18 – 21, 2000.
2. H. Sun and J. E. Mark "*Preparation and Some Mechanical Properties of Microcellular* Polysulfone Foams", *Polymer Preprints*, **42 (1)**, 634, 2001.
3. H. Sun, G. S. Sur, G. Beaucage and J. E. Mark "*Preparation and Properties of Nanocomposites Based on Polysulfone and an Organoclay*", *Polymer Preprints*, **42 (1)**, 630, 2001.

J. E. Mark awards and honors during the total grant period
Turner Alfrey Visiting Professorship (2001)
Paul J. Flory Polymer Education Award, ACS Division of Polymer Chemistry (2000)
Goodyear Medal, ACS Rubber Division (1999)

TRANSITIONS
PI's: Professor James E. Mark, University of Cincinnati, and Dr. Seng C. Tan, Wright Materials Research Co., 1948 Woodman Center Dr., Kettering, OH 45420

INVENTIONS
A patent application describing a new foaming technique will be filed by Wright Materials Research Co. (WMR). The claims will consist of the following items:

1. High-performance polymer poly(etherketoneketone)(PEKK) can be successfully foamed by this foaming process.
2. Very rigid molecular composites, such as PBZT/PEKK, SPBI/PVP can also be foamed by WMR using a new modified foaming technique. The densities of these molecular composite foams can be controlled from high to intermediate, through modification of the foaming conditions.
3. These molecular composite foams have superior mechanical and thermal properties compared to the conventional high temperature foams widely used in the aircraft industry.
4. Very uniform microcellular foams can be prepared from some other high-temperature high-performance polymer matrices, such as polysulfone (PSF), poly(ethersulfone) (PESF), poly(phenylsulfone) (PPSF) and poly(etherimide) (PEI) by a two-step batch foam process.
5. Molecular composites based on functionalized PSF and PBI can be synthesized through ionic-ionic interactions between polymer pairs. No phase separation was found on the

nanoscale level in these molecular composites, and the glass transition temperature and thermal stability can be greatly increased by the incorporation of the rigid-rod polymer.

6. Thin films cast from a solution of these molecular composites can also be foamed with very good microcellular structures using the new two-step batch-foaming process.

Samples of high-temperature polymers rigid-rod polymers were prepared at the Wright Patterson Air Force Base (WPAFB) for transitioning to Dr. Seng C. Tan, Wright Materials Research Co. (WMRC). These polymers were included as reinforcing agents in foamed polymer matrices. The resulting samples were sent to the University of Cincinnati (UC), where their mechanical properties were characterized by compression measurements to failure. In addition, their pore sizes and morphology in general were characterized at UC by scanning electron microscopy. The results obtained were interpreted jointly between the groups at WMRC, UC and WPAFB. The results are being written up as joint publications for standard refereed journals, generally in the field of polymers or materials science.

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PRESENTATIONS

At the American Chemical Society National Meetings leading to the Preprints cited above.
At the three AFOSR "Polymer Matrix Composite" Program Reviews held in Long Beach, CA during the total period of the grant..